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(54) Titre : UTILISATION D'HYDROGENE POUR REGENERER DES SORBANTS DE SULFURE D'HYDROGENE D'OXYDE METALLIQUE

(54) Title: THE USE OF HYDROGEN TO REGENERATE METAL OXIDE HYDROGEN SULFIDE SORBENTS

(57) Abrégé/Abstract:
A process to regenerate metal oxide desulfurization sorbents using hydrogen gas. The sorbents may be mono- or multi-metallic in nature, and preferably comprise Ni and/or Co. If desired, secondary metals may be incorporated to increase regeneration efficiency and/or capacity. Other additives suppress hydrocarbon craking.

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(54) Title: THE USE OF HYDROGEN TO REGENERATE METAL OXIDE HYDROGEN SULFIDE SORBENTS

(57) Abstract: A process to regenerate metal oxide desulfurization sorbents using hydrogen gas. The sorbents may be mono- or multi-metallic in nature, and preferably comprise Ni and/or Co. If desired, secondary metals may be incorporated to increase regeneration efficiency and/or capacity. Other additives suppress hydrocarbon craking.

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THE USE OF HYDROGEN TO REGENERATE METAL OXIDE HYDROGEN SULFIDE SORBENTS

CROSS REFERENCE TO RELATED APPLICATIONS

The present application is a continuation-in-part of USSN 09/326,827, filed June 7, 1999, which is a continuation-in-part of USSN 08/918,641, filed August 22, 1997, issued July 20, 1999 as U.S. Patent No. 5,925,239, which claims the benefit of Provisional Application SN 60/024,737.

FIELD OF THE INVENTION

[0001] This invention relates to a process for regenerating metal oxide hydrogen sulfide sorbents using hydrogen gas. The sorbents may be mono- or multi-metallic sorbents.

BACKGROUND OF THE INVENTION

[0002] The removal of sulfur from feedstocks is a fundamental process of the refining and petrochemical industries. One process for removing sulfur from a feedstock is hydrodesulfurization. Hydrodesulfurization involves the reaction of sulfur in the feedstock with hydrogen over supported noble metals, such as Pt, Pd, or non-noble metal sulfides, especially Co/Mo and Ni/Mo catalysts, at fairly severe temperatures and pressures to form hydrogen sulfide. The performance of the hydrodesulfurization catalysts can be inhibited by the presence of hydrogen sulfide. The use of sorbents to remove hydrogen sulfide produced during desulfurization improves the effectiveness of the overall hydrodesulfurization process.

[0003] The performance of a hydrogen sulfide sorbent depends upon a variety of properties. Thermodynamics and kinetics of sulfidation clearly are important, for they determine the overall sulfur capacity before breakthrough at some predetermined level of H_2S. Other important sorbent properties include stability and regenerability in extended use, the operating conditions required for regeneration, and the composition of the regeneration off-gas, which largely determines the choice of a downstream sulfur recovery process.

[0004] A practical limitation on the use of any hydrogen sulfide sorbent is the ability to regenerate the sorbent. Zinc oxide, one of the most promising and widely studied sorbents, has a very high equilibrium constant for sulfidation, but it is difficult to regenerate zinc oxide after use as a sorbent for hydrogen sulfide. The scope and applicability of such sorbents may, therefore, be limited by economic constraints relating to the level of sulfur being processed, the reactor volumetrics required, and issues pertaining to removal and disposal of the spent sorbent. These limitations are relieved if the hydrogen sulfide sorbent is capable of multicycle operation made possible by a means for regenerating the sorbent.

[0005] Spinels and zeolite-based materials are regenerable hydrogen sulfide sorbents; however, these materials are especially suited to the removal of hydrogen sulfide from gas streams where process temperatures are limited, preferably to about 75-125°C. These materials are inefficient for the capture of hydrogen sulfide at the higher temperatures used in conventional hydrodesulfurization technology.

[0006] Clinoptilolite molecular sieves also are regenerable; however, the temperatures at which clinoptilolite molecular sieves typically are treated also are relatively low. Clinoptilolite molecular sieves are used to remove hydrogen sulfide from C_4 to C_{12} feedstreams at temperatures of from about 90°C to about 260°C. Spent clinoptilolite molecular sieves are regenerated with a purge gas at temperatures of about 150°C to about 370°C.

[0007] Regenerable solid sorbents currently used for treating hot gaseous streams are typically based on metal oxides and are regenerated under oxidizing conditions at temperatures frequently greater than about 600°C. The regeneration of these sorbents using an oxidizing atmosphere requires an initial displacement of combustible organics and hydrogen, which not only is costly, but can be hazardous, especially at such high temperatures.

[0008] There is still a need in the art for methods that are capable of regenerating a variety of hydrogen sulfide sorbent materials.

SUMMARY OF THE INVENTION

[0009] The present invention provides a process for regenerating a hydrogen sulfide sorbent having a first cycle capacity, which process comprises exposing the spent hydrogen sulfide sorbent to a gas comprising a regenerating concentration of hydrogen under conditions effective for the hydrogen to regenerate the spent hydrogen sulfide sorbent, thereby producing a regenerated sorbent having a regenerated capacity substantially the same as the first cycle capacity.

DETAILED DESCRIPTION OF THE INVENTION

[0010] The present invention uses a reducing atmosphere, instead of an oxidizing atmosphere to regenerate solid hydrogen sulfide sorbents. The reducing atmosphere preferably comprises hydrogen gas, either alone or in combination with an inert gas, preferably nitrogen.

[0011] The regenerable sorbents of the present invention are preferably oxides of at least one metal selected from Fe, Ni, Co, and Cu. In a preferred embodiment, the metal is selected from the group consisting of Ni, Co, and a combination thereof. Examples of suitable supported metal and metal oxide based regenerable hydrogen sulfide sorbents include, but are not necessarily limited to: 5 Co/Al_2O_3; 10 Co/SiO_2; 20 Co/TiO_2; 20 Co/ZrO_2; 5 Ni/Al_2O_3; 10 Ni/SiO_2; 20 Ni/ZrO_2; 5

Cu/Al_2O_3; 10 Cu/SiO_2; 20 Cu/ZrO_2; 5 Fe/Al_2O_3; 10 Fe/SiO_2; 20 Fe/ZrO_2; 5 Co-5 Cu/Al_2O_3; 10 Co-10 Cu/ SiO_2; 10 Ni-5 Cu/ SiO_2; 20 Ni-2 Cu/ZrO_2; 10 Co-2 Pt/ Al_2O_3; 10 Co-5 Pd/SiO_2; 10 Co- 1 Sn/Al_2O_3; 20 Ni-4 Sn/SiO_2, wherein the numbers refer to the wt.% of metal, based on the total weight of the sorbent.

[0012] The sorbent may be employed as a bulk metal oxide or as a bulk metal, including but not necessarily limited to, a finely divided skeleton metal, including Raney metals, ponderous metals, Rieke metals, and metal sponges.

[0013] The sorbent may be supported on an inorganic support material in order to increase, for example, surface area, pore volume, and/or pore diameter. Suitable support materials are inorganic oxide support materials including, but not necessarily limited to, alumina, silica, zirconia, carbon, silicon carbide, kieselguhr, amorphous and crystalline silica-aluminas, silica-magnesias, aluminophosphates, boria, titania and combinations thereof. Preferred support materials include alumina, zirconia, and silica. The metal(s) or metal oxide(s) may be loaded onto these supports by conventional techniques known in the art. Such techniques include impregnation by incipient wetness, adsorption from excess impregnating medium, and ion exchange. In a preferred embodiment, the regenerable sorbents are prepared by conventional impregnation techniques using aqueous solutions of metal halides, oxides, hydroxides, carbonates, nitrates, nitrites, sulfates, sulfites, carboxylates and the like. The metal or metal oxide loadings may vary with the quantity of sulfur to be adsorbed per cycle, the cycle frequency, and the regeneration process conditions and hardware. Metal loadings range from about 2 wt.% to about 80 wt.%, preferably from about 3 wt.% to about 60 wt.%, and more preferably from about 5 wt.% to about 50 wt.%, based on the total weight of the regenerable sorbent.

[0014] After impregnation onto a support, the sorbent typically is dried, calcined, and reduced; the latter may either be conducted *ex situ* or *in situ*, as preferred. The regenerable sorbent may comprise a single metal or two or more metals. Certain metal combinations offer improved capacity, regenerability, and operability over the use of the individual metals. For bi- and polymetallic sorbents, similar ranges apply to each component; however, the loading may be either balanced or unbalanced, with the loading of one metal being greater than or less than the other.

[0015] Regeneration of the metal sorbent, particularly Ni and Co based sorbents, may be facilitated by including in the sorbent a regeneration-enhancing agent that catalyzes the reduction reaction required to restore the sorbent to its initial, active condition. Such agents include, but are not necessarily limited to, the noble metals of Group VIII of the Periodic Table of the Elements, preferably a noble metal selected from the group consisting of Ir, Pt, Pd, and Rh. The addition of from about 0.01 wt.% to about 10 wt.% of one of these metals benefits regenerability of the sorbent by decreasing the regeneration period and/or decreasing the regeneration temperature. Co-Ni bimetallic sorbents also experience more complete regeneration than the corresponding Ni only sorbent.

[0016] In addition to their activity as hydrogen sulfide sorbents, Fe, Co, and Ni also are hydrocracking active metals. Unless their hydrocracking activity is suppressed, these metals can cause hydrocracking of the other hydrocarbon stream being treated, leading to the production of low value light gas. The hydrocracking activity of the sorbent metal can be suppressed by incorporating from about 1 wt.% to about 10 wt.% (based on the weight of the sorbent), preferably from about 1.5 wt.% to about 7 wt.%, and most preferably from about 2 wt.% to about 6 wt.%, of a metal selected from Group IB or Group IVA of the Periodic Table of the Elements, such as Cu, Ag, Au, Sn, or Pb, preferably Cu. The Periodic Table of the Elements referred to herein appears on the inside cover page of the Merck Index, Twelfth Edition, Merck & Co., 1996. Hydrogenolysis also can be suppressed by incorporating a small amount, preferably from about 0.01 wt.% to about 1 wt.%, of one or more of the elements selected from Group VIA of the Periodic Table of the

Elements.

[0017] Accordingly, the sorbent may be presulfided by conventional methods such as exposing the virgin sorbent to dilute hydrogen sulfide in hydrogen at a temperature of from about 200°C to about 400°C for about 15 minutes to about 15 hours, or until sulfur breakthrough is detected. Sulfur levels of the presulfided sorbent will range from about 0.01 to about 1.0 wt.%, preferably from about 0.02 to about 0.7 wt.%, and more preferably from about 0.02 to about 0.5 wt.%, based on the total weight of the sorbent. Alternately, sulfur is incorporated by exposing the sorbent, preferably a virgin sorbent, to a dilute aqueous solution of from about 1 to about 10% sulfuric acid under impregnation conditions.

[0018] When desired, the regeneration-enhancing agent and the hydrogenolysis suppressor may be incorporated into the sorbent at the same time as the sorbent metal or later. Conventional methods such as impregnation may be employed.

[0019] Regeneration of the sorbent by a reducing environment generally requires more severe temperatures than those employed during a hydrodesulfurization (HDS) reaction. Typical regeneration temperatures range from about 100°C to about 700°C, preferably from about 250°C to about 600°C, and most preferably from about 275°C to about 550°C. The regeneration process is operable over a range of temperatures and pressures consistent with the intended objectives in terms of product quality improvement and consistent with any downstream process with which this invention is combined in either a common or sequential reactor assembly. Operating pressures may range from about 0 to about 3000 psia, preferably from about 50 to about 1000 psia, at H_2 gas rates of from about 10 to about 2,000 standard cubic feet per hour per pound (SCF/hr/lb) of sorbent, preferably about 20 to about 1500 SCF/hr/lb of sorbent, and more preferably about 100 to about 1000 SCF/hr/lb of sorbent.

[0020] Hydrogen is preferred for the regeneration process of the present invention and may be supplied pure or admixed with other passive or inert gases as is frequently the case in a refining or chemical processing environment. It is preferred that the hydrogen stream be substantially sulfur free, which can be achieved by conventional technologies. The regeneration stream will contain from about 50% to about 100% hydrogen, preferably from about 70 to about 100% hydrogen, and more preferably from about 80 to about 100% hydrogen, with any remainder being inerts or saturated light hydrocarbon gases.

[0021] Among the properties desired in a regenerable hydrogen sulfide sorbent are capacity to absorb hydrogen sulfide, regenerability, and the retention of both qualities over multicycle adsorption-regeneration sequences. Although it is preferred that both capacity and regenerability for a given sorbent approach about 100%, it is understood that this level is not a requirement for an effective regenerable sorbent. A capacity and regenerability that allow a frequency of regeneration that is reasonable and compatible with the overall process objective are acceptable and adequate. With this qualification in mind, an "effective regenerated capacity" is from about 5% to about 100%, by weight, of a first cycle capacity, preferably from about 10% to about 100% of a first cycle capacity, most preferably from about 20% to about 100% of a first cycle capacity. A "first cycle capacity" refers to the sorbent hydrogen sulfide capacity of a fresh or "virgin" sorbent material.

[0022] In a preferred embodiment, the sorbent is used in conjunction with distillate and naphtha hydrodesulfurization (HDS) processes, preferably the processes described in U.S. Patents 5,925,239, 5, 928,498, and 5,935,420, all incorporated herein by reference. Typical hydrodesulfurization conditions include temperatures from about 40°C to about 500°C (104 - 930°F), preferably about 200°C to about 450°C (390 - 840°F), and more preferably about 225°C to about 400°C (437 - 750°F). Operating pressures include about 50 to about 3000 psig, preferably 50 to about 1200 psig, and more preferably about 100 to about 800 psig at gas rates of about 50 to about 10,000 SCF/B, preferably about 100 to about 7500 SCF/B, and more preferably about 500 to about 5000 SCF/B. The liquid hourly space velocity may be varied over the range of about 0.1 to about 100 V/V/Hr, preferably about 0.3 to about 40 V/V/Hr, and more preferably about 0.5 to about 30 V/V/Hr. The liquid hourly space velocity is based on the volume of feed per volume of catalyst per hour, i.e., V/V/Hr.

[0023] Various sorbent bed configurations may be used in the practice of the present invention. Examples of suitable bed configurations include, but are not necessarily limited to bubbling beds, fixed beds operated in a cocurrent or countercurrent mode, non-fluidized moving beds, fluidized beds, or a slurry of HDS catalyst and sorbent in a continuously stirred tank reactor ("CSTR"), or slurry bubble column. Fluidized beds may be advantageous in conjunction with processes where continuous regeneration of the sorbent is needed. In addition, flow-through, fluidized bed technology which includes a disengaging zone for catalyst and sorbent may be useful to regenerate sorbent particles. The process can operate under liquid phase, vapor phase or mixed phase conditions. It should be noted that the HDS catalyst and the sorbent may be separate particles, a composite of HDS catalyst and sorbent, and an HDS catalyst impregnated onto a sorbent. However, when the sorbent and HDS catalyst are arranged so that the HDS catalyst is present during sorbent reduction, undesirable desulfiding of the HDS catalyst may result. In such cases, it would be desirable to adjust the sorbent reduction conditions to abate the affects of HDS catalyst desulfurization, or to subject the HDS catalyst to a re-sulfiding step prior to re-use, or to employ an HDS catalyst that does not require sulfiding, such as a noble metal HDS catalyst. The HDS catalyst may be re-sulfided by contacting the catalyst with the sulfur-containing hydrocarbon feed.

[0024] Fixed bed configurations may be operated in either of cocurrent and countercurrent modes, i.e., with hydrogen-containing treat gas flowing over the

HDS catalyst in the same or opposite direction as the sulfur-containing feed. In another embodiment, the hydrogen-containing treat gas is employed in a "once-through" arrangement is, therefore, not recycled. Countercurrent HDS arrangements may be preferred in cases where increased contacting between the surfur-containing feed, treat gas, and catalyst would be desired and in cases where increased H_2S stripping would be beneficial. Fluidized beds may be advantageous in conjunction with processes where continuous regeneration of the sorbent is needed. In addition, flow-through, fluidized bed technology which includes a disengaging zone for catalyst and sorbent may be useful to regenerate sorbent particles.

[0025] Those skilled in the art are aware that the choice of bed configuration for an HDS catalyst and a sorbent depends upon the objective of the overall process, particularly when the process is integrated with one or more subsequent processes, or when the objective of the overall process is to favor the selectivity of one aspect of product quality relative to another. However, it is preferred that the sorbent not be placed upstream of the HDS catalyst.

[0026] A preferred embodiment uses a stacked bed configuration with a swing reactor designed to permit regeneration of spent sorbent while a fresh sorbent is placed in service. In a stacked bed configuration, the HDS catalyst is stacked, or layered, above and upstream of the sorbent. The stacked beds may either occupy a common reactor, or the HDS catalyst may occupy a separate reactor upstream of the reactor containing the sorbent. This dedicated reactor sequence is preferred when the HDS catalyst and the sorbent require different reactor temperatures.

[0027] In another embodiment, the sorbent and the HDS catalyst are used in a mixed bed configuration. In this configuration, particles of the HDS catalyst are intimately intermixed with those of the sorbent. In both the stacked bed and the mixed bed configurations, the HDS catalyst particles and the sorbent particles may be of similar or identical shapes and sizes. The particles of one component may also differ, for example, in shape, density, and/or size from the particles of the second component. The use of particles having different sizes may be employed when, for example, is simple physical separation of the bed components upon discharge or reworking.

[0028] In yet another embodiment, the two components are blended together to form a composite particle incorporating both the HDS catalyst and the sorbent or individual discrete components. For example, a finely divided, powdered Pt on alumina HDS catalyst is uniformly blended with a regenerable sorbent and the mixture is formed into a common catalyst particle. Or, the regenerable sorbent may be incorporated into the support, and Pt, for example, may be impregnated onto the sorbent containing support, such as alumina.

[0029] In another two component configuration, an alumina support is impregnated with an HDS metal or metals and a sorbent on a common base. Both metals may be distributed uniformly throughout the catalyst particle, or the sorbent and/or HDS components may be deposited preferentially on the outside of the particle to produce a rim, or eggshell, sorbent or HDS rich zone.

[0030] A three component bed configuration also may be used. In one embodiment, denoted as mixed/stacked, a mixed HDS catalyst/ sorbent bed is configured upstream of a single HDS/hydrogenation catalyst. In another embodiment, known as a stacked/stacked/stacked configuration, the three components are layered from top to bottom as follows: HDS catalyst/sorbent/HDS catalyst. In one embodiment, three component systems may occupy a common reactor. In another embodiment, a three component system may be used in a two-reactor train in which the HDS catalyst/sorbent occupy a lead reactor in a mixed or stacked configuration and a HDS catalyst occupies the tail reactor. This arrangement allows for the operation of two reactor sections at different process conditions, especially temperature, and imparts flexibility in controlling process parameters such as selectivity and/or product quality.

[0031] The composition of the bed is independent of configuration and may be varied in accordance with the specific or integrated process to which the invention is applied. If the capacity of the sorbent is limiting, the composition of the bed must be consistent with the expected lifetime, or cycle, of the process. These parameters are in turn sensitive to the sulfur content of the feed being processed and to the degree of desulfurization desired. For these reasons, the composition of the bed is flexible and variable, and the optimal bed composition for one application may not serve an alternative application equally well. In general, the weight ratio of the sorbent to the hydrodesulfurization catalyst may range from about 0.01 to about 1000, preferably from about 0.5 to about 40, and more preferably from about 0.7 to about 30. For three component configurations, these ranges apply to the mixed zone of the mixed/stacked arrangement and to the first two zones of the stacked/stacked/stacked design. The hydrodesulfurization catalyst present in the final zone of these two arrays is generally present at a weight ratio that is equal to or less than the combined weight compositions of the upstream zones.

[0032] The process may be used as a stand-alone process for, for example, fuels, lubes, and chemicals applications. Alternately, the process may be combined and integrated with other processes in a manner so that the net process affords product and process advantages and improvements relative to the individual processes not combined. The following embodiments are included to illustrate, but not limit, uses for the processes of this invention.

[0033] Processes relating to fuels processes include: desulfurization of gasoline range feed and product streams; desulfurization of distillate streams; desulfurization of FCC streams preceding recycle to 2nd stage process; desulfurization of hydrocracking feeds; multi-ring aromatic conversion through selective ring opening; aromatics saturation processes; hydroisomerization; sulfur removal from natural, synthesis, and recycle gas streams and from field condensate streams. Processes relating to the manufacture of lubricants include: hydrocracking, product quality improvement through mild finishing treatment; optimization of white oil processes by decreasing catalyst investment and/or extending service factor. Processes relating to chemical processing include: substitute for environmentally unfriendly nickel based hydroprocesses; preparation of high quality feedstocks for olefin manufacture through various cracking processes and for the production of oxygenates by oxyfunctionalization processes; production of solvent and polymer grade olefins and aromatics.

[0034] This invention is illustrated by, but not limited to the following examples, in which the following experimental conditions were used unless otherwise indicated:

GENERAL CONDITIONS

[0035] The capacity and hydrogen regenerability of the hydrogen sulfide sorbents were assessed using a Cahn TG 121 Thermogravimetric Analyzer using nominally equivalent weight charges of each sorbent. The candidate sorbents were initially calcined in air at 400°C for 3 hr prior to being placed in the analyzer. The sorbent was heated at 500°C for 1 hr in hydrogen and then cooled to 325°C and exposed to a gas blend containing 1000 vppm H_2S in H_2 for a period of 2 hr during which interval the weight gain associated with the adsorption of H_2S was recorded. The spent sorbent subsequently was heated to 500°C in H_2 for one hour and to 550°C for one hour during which interval the desorption of H_2S, or the regeneration of the sorbent, was noted. In multicycle testing this sequence was duplicated as noted to simulate repetitive adsorption-regeneration cycles. Regenerability was further confirmed by the observation of phase changes using a controlled environment, high temperature cell mounted on a X-ray diffractometer.

[0036] The sorbents were prepared by incipient wetness impregnation of the various support materials with aqueous solutions of the metal nitrates. The extrudates were air dried under vacuum at 120°C for 24 hr. Calcination in flowing air was carried out in a small catalyst pretreat unit or in a thermogravimetric unit dedicated to this function. In both cases the calcination was conducted at 400°C for 3 hr. All sorbent compositions in the examples are nominal wt. % metal on support.

EXAMPLE I

[0037] This experiment compared zinc oxide (a non-hydrogen regenerable sorbent) as a control to supported Fe, Co, Ni, and Cu sorbents.

Sample No.	Sorbent	Sulfur Gain, Wt. %	Regeneration, %
1	ZnO	8.0	0
2	10 Fe/ZrO_2	5.3	45
3	10 Co/ZrO_2	4.9	95
4	10Ni/ZrO_2	3.5	73
5	20Ni/ZrO_2	6.1	79
6	20 Cu/ZrO_2	4.3	63
7	17Co/TiO_2	8.9	28

[0038] % Regeneration refers to the percent of chemisorbed sulfur removed from the sorbent during regeneration. If no sulfur is released during regeneration, this value is zero. Total removal of sulfur during regeneration corresponds to 100% regeneration.

[0039] The results demonstrate that Fe, Co, Ni, and Cu were active hydrogen sulfide sorbents and were capable of being regenerated by hydrogen to varying degrees. Co and Ni were more regenerable than Fe and Cu on a common support. Metal loading (Samples 4 and 5) exerted an influence on capacity but not on regenerability. Titania (Sample 7) was least preferred as a support although the degree of regenerability was within the limits of this invention.

EXAMPLE II

[0040] Experiments were done to determine what factors had an impact on capacity and regenerability.

Sample No.	Sorbent	Sulfur Gain, Wt.%	Regeneration, %
8	20 Co/SiO_2	7.8	98
9	20 Co/Al_2O_3	7.6	99
10	20 Co/ZrO_2	8.0	73
11	10 Co/ZrO_2	4.9	95
12	10 Co/SiO_2	4.1	100
13	10 Co/Al_2O_3	4.1	100

[0041] Samples 8-13 illustrate that, for a common metal, capacity and percent regeneration were independent of support for the supports shown. As expected, capacity was a function of metal loading, but degree of regeneration was not influenced by total metal content. Samples 14-15 and 16-18 illustrate that for Co on a common support, the hydrogen sulfide capacity of the sorbent was a function of metal content, but that the kinetics of hydrogen regeneration were insensitive to metal loading.

Sample No.	Sorbent	Sulfur Gain, Wt.%	Regeneration Rate, mg/hr
14	10 Co/ZrO_2	4.9	0.4
15	20 Co/ZrO_2	8.0	0.4
16	5 Co/Al_2O_3	2.3	0.5
17	10 Co/Al_2O_3	4.1	0.6
18	20 Co/Al_2O_3	7.6	0.6

Regeneration Rate = mg of sulfur removed per hour during hydrogen regeneration.

EXAMPLE III

[0042] The hydrogen sulfide sorbent of Sample 5 (Example I) was subjected to multicycle adsorption-regeneration by the procedure described above. The 20 Ni/ZrO_2 sorbent was subject to five complete cycles without significant loss of hydrogen sulfide capacity and hydrogen regenerability. The sulfur weight gain and degree of regenerability were near parity with the values of Sample 5.

EXAMPLE IV

[0043] The hydrogen sulfide sorbent of Sample 17 (Example II) was subjected to multicycle adsorption-regeneration by the procedure described above. The 10 Co/Al_2O_3 sorbent was subject to six complete cycles without significant loss of hydrogen sulfide capacity and hydrogen regenerability. The sulfur weight gain and degree of regenerability were at parity with the values of Sample 17.

EXAMPLE V

[0044] A 1.0 g sample of the 10 Co/Al_2O_3 sorbent of Sample 17 (Example II) was diluted with 30 g of inerts and charged to a flow-through, fixed bed reactor. The sorbent was reduced in hydrogen at 500°C for 1 hr and was then subjected to a blend of 1000 vppm H_2S in H_2 at 300°C and a gas flowrate of 50 ml/min. The hydrogen stream exiting the sorbent bed was monitored for H_2S content using a H_2S detector, which measured the breakthrough time approximating complete saturation of the sorbent. The sorbent was evaluated in this manner in three distinct tests, which are summarized below.

Test Sorbent	Breakthrough Time, hr	Sorbent S Content, Wt.%
1	9.8	3.1
2	9.7	2.9
3	9.2	2.6

[0045] The calculated sulfur value for the conversion of the sorbent Co content to Co_9S_8 was 3.0 wt.%. The data in the preceding table confirm the TGA results in a fixed bed configuration and indicate reproducible and efficient utilization of the sorbent capacity.

EXAMPLE VI

[0046] The procedure of Example V was followed except that the sorbent consisted of three independent zones separated by inerts, each zone containing the 10 Co/Al_2O_3 sorbent diluted with inerts. Hydrogen sulfide breakthrough occurred with this bed at 29.3 hr., a period about three times that seen for a single sorbent zone. Each zone was separated and analyzed for sulfur; the sulfur values for the top, middle, and bottom zones were 3.1, 3.3, and 3.3 wt.%, respectively. These values reflect highly efficient operation of the sorbent.

EXAMPLE VII

[0047] The procedure of Example VI was repeated using the three zone sorbent bed as described. After H_2S breakthrough was detected at 27 hr, the sorbent bed was regenerated with hydrogen at 500 ml/min at 450°C for 3 hr, 500°C for 3 hr, and finally at 550°C for 10 hr. The three sorbent zones were separated and analyzed for sulfur; the sulfur values for the top, middle, and bottom zones were 0.2, 0.2, and 0.2 wt.%, respectively. These sulfur values demonstrate hydrogen regeneration of the total sorbent bed at a level of about 95% regeneration efficiency.

EXAMPLE VIII

[0048] The procedure of Example VIII was repeated using a single sorbent zone.

After H_2S breakthrough was detected, the bed was regenerated with hydrogen. The sorbent was then cooled to 300°C and exposed to the dilute H_2S in H_2 stream. The adsorption-regeneration cycle was repeated for four cycles at the conclusion of which the sorbent was sulfided a final time. The results are summarized in the following table.

Cycle #	Breakthrough Time, hr	Sorbent S Content, Wt %
1	10.5	n/a
2	13.6	n/a
3	14.3	n/a
4	14.2	3.1

[0049] The breakthrough value times indicate successful and efficient regeneration of the sorbent following each exposure to H_2S. If essentially complete regeneration per cycle were not occurring, a significant decrease in breakthrough time for each succeeding cycle would be expected. The sulfur content of the sorbent illustrated that the sulfur capacity was unimpaired after multicycle service.

EXAMPLE IX

[0050] The 10 Co/Al_20_3 sorbent of Sample 17 (Example II) was subjected to dilute H_2S in H_2 as described previously. After H_2S breakthrough was detected, the sorbent was regenerated using variations in the H_2 treat rate, temperature and time as shown in the following table. The results indicate that the regeneration period is a function of these process variables and that these may be selected to maintain the degree of regeneration and/or the regeneration period required to reach a specified regeneration efficiency.

Regen #	Breakthr. Time, hr	H_2 Flowrate, ml/min	1st, °C-hr	2nd, °C-hr	3rd, °C-hr	Sorbent S, Wt. %
1	12.5	900	450-3	500-3	550-10	0.2
2	13.0	300	450-3	500-3	550-10	0.2
3	14.1	300	450-3	500-3	550-3	0.2
4	13.8	300	450-1	500-1	550-1	1.5
5	14.5	500	450-1	500-1	550-1	0.3

EXAMPLE X

[0051] Experiments were performed to determine whether a combination of metals in the sorbent had an impact on the regeneration achieved. The results are given in the following table:

Sample No.	Sorbent	Sulfur Gain, Wt. %	Regeneration,%
Reference	10 Co/Al_2O_3	4.1	100
Reference	10 Ni/ZrO_2	3.5	73
19	5 Co-15 Ni/SiO_2	7.3	90
20	10 Co-10 Ni/SiO_2	7.4	100
21	15 Co-5 Ni/SiO_2	7.9	100
22	20 Co-1.5 Re/Al_2O_3	7.4	100
23	20 Co-5 Re/SiO_2	6.6	100
24	20 Co-5 Re-2 Pt/SiO_2	5.3	100
25	10 Co-2 Ru/SiO_2	4.1	100
26	10 Co-2 Pd/SiO_2	4.3	100
27	10 Co-2 Pt/SiO_2	3.0	100

[0052] Samples 19-21 show that a set of Co-Ni based sorbents, where the total metal loadings is equivalent but the ratio of Co to Ni is varied, shared a common sulfur capacity and regeneration efficiency. The sulfur capacities agreed with those predicted by the monometallic sorbents, but the Co-Ni bimetallic sorbents unexpectedly experienced more complete regeneration than the corresponding Ni only sorbent.

[0053] Samples 22-24 illustrate that the Co-Re sorbents had reasonable sulfur capacity, which declined with increasing Re loading due to a decrease in the rate of reaction with H_2S (not shown) which limited sulfur uptake within a fixed period of time. The Co-Re sorbents were readily regenerable with hydrogen as the data indicate.

[0054] Samples 25-27 demonstrate that the incorporation of Group VIII noble metals did not impair the sulfur capacity of Co although the rate of sulfur uptake was retarded in the presence of Pt. Hydrogen regeneration of these bimetallic sorbents occurred readily with essentially quantitative recovery of fresh sorbent capacity.

EXAMPLE XI

[0055] A 1.0 g sample of various bimetallic sorbents was diluted with 30 g of inerts and charged to a flow-through, fixed bed reactor. The sorbent was reduced by hydrogen at 500°C for 1 hr and then was subjected to a blend of 1000 vppm H_2S in H_2 at 300°C and a gas flowrate of 50 ml/min. The hydrogen stream exiting the sorbent bed was monitored for H_2S content using a H_2S detector, which measured the breakthrough time approximating complete saturation of the sorbent.

[0056] After the initial breakthrough of H_2S was detected, the sorbent bed was regenerated in H_2 flowing at 300 ml/min using temperature-time programs of 450°C for 3 hr, 500°C for 3 hr, and finally 550°C for 3 hr. This absorption-regeneration sequence was repeated to simulate two or three complete cycles. The residual sulfur content of the sorbent following the second regeneration was measured analytically. The results are given in the following table:

Sample	Sorbent	Breakthrough Time, hr, #-Cycles	Sorbent S wt. %
Reference	10 Ni/ZrO_2	16.8 - 2	0.8
28	20 $Ni\text{-}2Cu/ZrO_2$	28.4 - 2	2.0
29	10 $Co\text{-}1\ Pt/SiO_2$	13.8 - 2	0.1
30	10 $Co\text{-}5\ Cu/SiO_2$	14.4 - 2	1.2
31	10 $Co\text{-}5\ Cu/SiO_2$	11.5 - 3	0.7

[0057] The breakthrough times for the second or third cycle sorbents are characteristic of the breakthrough period of fresh sorbent and indicate successful hydrogen regeneration of these bimetallic sorbents. If hydrogen regeneration were not occurring, the breakthrough period for the multicycle sorbents would be significantly decreased. The sulfur contents of the regenerated sorbents demonstrate that a degree of regeneration > 60% was achieved in all cases except for $Ni\text{-}Cu/ZrO_2$ where the rate of regeneration was slow relative to the remaining sorbents.

EXAMPLE XII

[0058] The Co/Al_2O_3 sorbent of Sample 13 (Example II) was subjected to a heptane cracking test to measure the hydrogenolysis activity of the sorbent as reflected in hydrocracking to methane. The same Co/Al_2O_3 sorbent was impregnated with dilute sulfuric acid to introduce 0.05 wt.% sulfur into the sorbent.

[0059] A sulfuric acid stock solution was prepared by diluting 1 mL. of concentrated sulfuric acid with 50 mL of deionized water. A solution of 0.5 mL sulfuric acid stock solution in 9.0 mL of deionized water was added dropwise with stirring to 10 g of a previously prepared 10% Co/Al_2O_3 sorbent. The sorbent was allowed to stand overnight and was charged to a reactor for calcination in air at 400°C for 3 hours. The material was converted to 14-35 mesh. Anal: Co 9.91; S, 0.055 (wt.%).

[0060] The sulfided sorbent was subjected to a heptane cracking test to measure the hydrogenolysis activity of the sorbent as reflected in hydrocracking to methane. The same Co/Al_2O_3 sorbent also was impregnated with dilute sulfuric acid to introduce 0.25 wt.% sulfur into the sorbent. The sulfided sorbent was subjected to a heptane cracking test to measure the hydrogenolysis activity of the sorbent as reflected in hydrocracking to methane. The results appear in the table below.

Hydrogenolysis Activity Of Unsulfided And Sulfided Co Sorbents
n-Heptane, 500 psig, 5 W/H/W, H_2/Oil = 6

Sample	32		33		34	
Sorbent	10 Co/Al_2O_3		10 Co-0.05 S/Al_2O_3		10 Co-0.25 S/Al_2O_3	
Reaction Temp. °C	300	325	300	325	300	325
Methane, wt. %	10.4	47.5	1.1	2.5	0.0	0.0

[0061] Examples II, IV, and V illustrate that supported Co sorbents are highly active for the capture of hydrogen sulfide, have high hydrogen sulfide capacity, and are capable of retained capacity following multicycle hydrogen regeneration. Sample 32 reveals that this sorbent is very active for hydrocracking feedstocks to light gas. Samples 33 and 34 demonstrate that this hydrocracking activity is greatly decreased and eliminated by the presence of low levels of sulfur.

EXAMPLE XIII

[0062] The procedure of Example II was repeated using the sulfur bearing Co/Al_2O_3 sorbents of Examples 33 and 34. The capacity of the sorbent for the capture of hydrogen sulfide was equal to that of Sample 13 in Example II indicating that the affinity of the sorbent for the capture of hydrogen sulfide was not impaired by the presence of low levels of sulfur.

EXAMPLE XIV

[0063] A 10 Co-10 Cu/SiO_2 sorbent was synthesized. A solution of 12.3 g of

$Co(NO_3)_2(6\ H_2O)$ and 9.6 g of $Cu(NO_3)_2(3\ H_2O)$ in 50 mL of deionized water was added dropwise with stirring to 25 g of SiO_2 extrudates contained in a small evaporating dish. The mixture was permitted to stand at room temperature until dry and was then dried under vacuum at 120°C for 24 hr. The sorbent was charged to a small catalyst pretreat unit and calcined in air at 400°C for 3 hour. The sorbent was converted to 14-35 mesh particles for testing. Anal: Co, 8.23 wt.%; Cu, 8.12 wt.%. Multicycle capacity and regenerability in service was demonstrated by TGA.

EXAMPLE XV

[0064] The following sorbents were subjected to a heptane cracking test to measure the hydrogenolysis activity of the sorbent as reflected in hydrocracking to methane: the Co/Al_2O_3 sorbent of Sample 13 (Example II); the Ni/ZrO_2 sorbent of Sample 5 (Example I); the Co/ZrO_2 sorbent of Sample 11 (Example II); and, the $Ni-Cu/ZrO_2$ sorbent of Sample 28 (Example XI); the $Co-Cu/ZrO_2$ sorbent of Sample 30 (Example XI); and a 10 Co-10 Cu/SiO_2 sorbent (Sample 35). The results appear in the following table:

Hydrogenolysis Activity Of Unsulfided And Sulfided Co Sorbents
n-Heptane, 500 psig, 5 W/H/W, H_2/Oil = 6

Sample	13	5	11	28	30	35
Sorbent	10 Co/ Al_2O_3	20Ni/ ZrO_2	10 Co/ ZrO_2	20Ni-2Cu/ ZrO_2	10Co-5Cu/ ZrO_2	10Co-10Cu/ SiO_2
Methane, Wt.%	47.5	75.0	85.0	5.0	0.0	0.0

[0065] Based on the foregoing, it was concluded that the hydrocracking activity of the monometallic sorbents is extremely high. This hydrogenolysis activity is effectively suppressed by the addition of a hydrogenolysis moderator. Neither the sulfur capacity nor the ability to be regenerated by treatment with hydrogen are compromised in these bimetallic catalysts relative to their monometallic analogs (Samples 28, 30).

EXAMPLE XVI

[0066] Experiments were performed to determine whether hydrogen regeneration could be augmented by adding, for example, a noble metal to the sorbent. The results appear in the following table:

Sample	Sorbent	Sulfur Gain, Wt. %	% Regenerated at 500° C for 1 hr
12	10 Co/SiO_2	4.3	47
36	10 Co-0.5 Pd/SiO_2	4.3	55
37	10 Co-1.0 Pd/SiO_2	4.4	59
26	10 Co-2.0 Pd/SiO_2	4.4	64
38	10 Co-5.0 Pd/SiO_2	4.4	65
39	10 Co-0.5 Pt/SiO_2	4.2	60
40	10 Co-1.0 Pt/SiO_2	3.9	70
27	10 Co-2.0 Pt/SiO_2	3.0	88
41	10 Co-1.0 Pt-1.0 Pd/SiO_2	3.9	74

[0067] Sample 12 exhibits the sulfur capacity typical of a supported 10% Co hydrogen sulfide sorbent. At conditions purposely selected to prevent complete regeneration by hydrogen treatment (500°C for 1 hr), the cobalt sorbent lost 47% of the adsorbed hydrogen sulfide, or is 47% regenerated. The addition of Pd (Samples 26, 36-38) had no influence on the sulfur capacity, but the presence of Pd clearly facilitated hydrogen regeneration at common conditions. The degree of regeneration increased with increasing Pd up to a level of about 2 wt.% Pd.

[0068] Samples 27, 39, 40 illustrate a similar trend with the presence of Pt, which is more effective than Pd at promoting the rate of hydrogen regeneration. The apparent loss of sulfur capacity at ~2 wt.% Pt is largely due to a decrease in the kinetics of sulfur pickup.

[0069] Sample 41, where Pt and Pd are present at equivalent wt.% loadings, but at differing atomic loadings, displays a synergism between the two noble metals yielding a more facile regeneration than either metal alone when present at 1 wt.%.

[0070] The data collectively illustrate that the hydrogen regeneration of a highly saturated hydrogen sulfide sorbent is promoted by the presence of one or more noble metals from Group VIII of the Periodic Table of the Elements. This promotional effect may be used either to shorten the regeneration period, to decrease the regeneration temperature, or both.

CLAIM IS:

1. A process for regenerating a hydrogen sulfide sorbent comprising:

providing a spent hydrogen sulfide sorbent having an effective quantity of a sorbent containing an oxide of at least one metal selected from Fe, Ni, Co, and Cu, said hydrogen sulfide sorbent having a level of sulfur defining a first cycle capacity for absorbing hydrogen sulfide; and exposing said spent hydrogen sulfide sorbent to a gas comprising a regenerating concentration of hydrogen under conditions effective for said hydrogen to regenerate said spent hydrogen sulfide sorbent, thereby producing a regenerated sorbent.

2. The process of claim 1 wherein said metal is at least one of Ni and Co.

3. The process of claim 2 wherein said conditions comprise a temperature from about 100°C to about 700°C.

4. The process of claim 3 wherein said conditions comprise a temperature from about 250°C to about 600°C.

5. The process of claim 2 wherein said spent hydrogen sulfide sorbent contains a regeneration rate enhancing amount of a noble metal selected from Group VIII of the Period Table of the elements, wherein said regeneration rate enhancing amount reduces said regenerated capacity by about 50% or less.

6. The process of claim 5 wherein said regeneration rate enhancing amount reduces said regenerated capacity by about 30% or less.

7. The process of claim 5 wherein the noble metal is at least one of Ir, Pt, Pd, and Rh.

8. The process of claim 7 wherein two noble metals are present.

9. The process of claim 5 wherein said regeneration rate enhancing amount

ranges from about 0.01 wt.% to about 10 wt.%.

10. The process of claim 1 wherein the sorbent further comprises at least one hydrocracking suppressor selected from Group IB, Group IVA, and Group VIA of the Periodic Table in a suppressing quantity sufficient to suppress hydrocracking.

11. The process of claim 10 wherein the hydrocracking suppressor is

(i) at least one of Cu, Ag, Au, Sn, and Pb, and the suppressing quantity ranges from about 1 wt.% to about 10 wt.%,

or

(ii) at least one Group VIA element, and the suppressing quantity ranges from about 0.01 wt.% to about 2 wt.%.

12. The process of claim 1 wherein the regenerated sorbent has a capacity for absorbing hydrogen sulfide ranging from about 5% to about 100% of the first cycle capacity.

13. A desulfurization process comprising:

(a) contacting a hydrocarbon containing sulfur with a catalytically effective amount of a catalyst system under catalytic hydrodesulfurization conditions, the catalyst system being comprised of:

(i) a hydrodesulfurization catalyst containing at least one of Mo, W, Fe, Co, Ni, Pt, Pd, Ir, and Rh; and comprising at least one of:

(ii) a hydrogen sulfide sorbent containing at least one sorbent metal selected from Fe, Co, Ni, and Cu, said hydrogen sulfide sorbent comprising a level of sulfur defining a first cycle capacity for absorbing hydrogen sulfide, said contacting producing at least a desulfurized product and a spent hydrogen sulfide sorbent; and then

(b) exposing said spent hydrogen sulfide sorbent to a gas comprising a regenerating concentration of hydrogen under conditions effective for said hydrogen to regenerate said spent hydrogen sulfide sorbent, producing a regenerated sorbent.

14. The process of claim 13 wherein said sorbent metal is at least one of Ni and Co.

15. The process of claim 13 wherein the regenerating conditions include a temperature ranging from about 100°C to about 700°C and a pressure ranging from about 0 psia to about 3000 psia.

16. The process of claim 15 wherein the regeneration concentration of hydrogen ranges from about 10 SCF/hr/lb to about 2000 SCF/hr/lb, based on the weight of the hydrogen sulfide sorbent.

17. The process of claim 14 wherein the hydrogen is combined with at least one inert or light hydrocarbon diluent gas, wherein the hydrogen is present in a volume ranging from about 50% to about 100%, based on the total volume of hydrogen and diluent, and wherein the regenerating conditions include a temperature ranging from about 100°C to about 700°C, at a pressure ranging from about 0 psia to about 3000 psia, for a time ranging from about 0.25 hour to about 10 hours, and a hydrogen treat gas rate of about 10 to about 2000 SCF/hr/lb, based on the weight of the hydrogen sulfide sorbent.

18. The process of claim 13 wherein the regenerated sorbent has a regenerated capacity for sulfur absorbtion ranging from about 5 wt.% to about 100 wt.% of the first cycle capacity.

19. The process of claim 17 wherein the hydrogen is combined with an inert diluent gas.

20. The process of claim 13 wherein the sorbent further comprises at least one hydrocracking suppressor selected from Group IB, Group IVA, and Group VIA of the Periodic Table in a suppressing quantity sufficient to suppress hydrocracking.

21. The process of claim 20 wherein the hydrocracking suppressor is

(i) at least one of Cu, Ag, Au, Sn, and Pb, and the suppressing quantity ranges from about 1 wt.% to about 10 wt.%,

or

(ii) at least one Group VIA element, and the suppressing quantity ranges from about 0.01 wt.% to about 2 wt.%.

22. The process of claim 13 wherein the hydrogen sulfide sorbent is the regenerated sorbent.

23. The process of claim 22 wherein steps (a) and (b) are performed continuously.

24. The process of claim 13 wherein at least one of the hydrodesulfurization catalyst and the hydrogen sulfide sorbent is supported on an inorganic refractory support.

25. The process of claim 13 wherein the weight ratio of the hydrogen sulfide sorbent to the hydrodesulfurization catalyst ranges from about 0.01 to about 1000.

26. The process of claim 25 wherein the hydrodesulfurization catalyst and the hydrogen sulfide sorbent are in the form of separate particles.

27. The process of claim 25 wherein the hydrodesulfurization catalyst and the hydrogen sulfide sorbent are in the form of a composited particle.

28. The process of claim 25 wherein the catalyst system is in the form of catalyst particles, and wherein the hydrogen sulfide sorbent is impregnated with the hydrodesulfurization catalyst.

29. The process of claim 13 wherein the hydrodesulfurization catalyst contains at least one of Fe, Co, Ni, Mo, and W.

30. The process of claim 13 operated in at least one of a moving bed, a bubbling bed, a non-fluidized moving bed, a fluidized bed, a continuously stirred tank reactor, and a slurry bubble column.

31. The process of claim 30 wherein the process is a fixed bed process operated in one of

(i) cocurrent

and

(ii) countercurrent mode, and

wherein the catalytic hydrodesulfurization conditions include a temperature of about 40°C to about 500°C, a pressure ranging from about 100 psig to about 3,000 psig, a treat gas rate ranging from about 50 to about 10,000 SCF/B, and a space velocity ranging from about 0.1 to about 100 V/V/Hr.