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(54) **METHOD FOR REMOVING MERCURY
FROM HYDROCARBON STREAMS**

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(57) **ABSTRACT**

Method of removing mercury from a mercury-comprising hydrocarbon stream, in which the hydrocarbon stream is brought into contact with an absorbent comprising copper on a support material, wherein the hydrocarbon stream is brought into contact with the absorbent in the presence of hydrogen.

METHOD FOR REMOVING MERCURY FROM HYDROCARBON STREAMS

[0001] The invention relates to a method of removing mercury and/or arsenic from a mercury-comprising hydrocarbon stream.

[0002] Mercury is present as impurity in numerous streams of materials which are obtained or processed in the chemical or petrochemical industry. These are often streams which are obtained in the processing or thermal utilization of fossil raw materials such as petroleum, natural gas or coal and in the utilization of wastes, since these raw materials or wastes comprise traces of mercury in elemental form or in chemically bound form. Streams comprising mercury as impurity are also obtained in processes in which mercury or mercury-comprising substances are used as reagent or catalyst. An example which may be mentioned is the electrolysis hydrogen obtained in the production of chlorine by the amalgam process. Because of the high toxicity of mercury, it is in most cases necessary to separate off this metal or compounds comprising this metal from the streams obtained in the processes concerned. Furthermore, mercury has the property of attacking apparatuses comprising aluminum by amalgam formation with destruction of the oxide layer on the surface of the aluminum, so that streams which pass through apparatuses or vessels made of aluminum have to be virtually mercury-free. In addition, catalysts comprising noble metals, as are used, for example, in petrochemical processes, are poisoned by traces of mercury.

[0003] In Fuel Processing Technology 82 (2003), pp. 89-165, J. H. Pavlish et al. give an overview of methods of removing mercury from the offgas streams obtained in coal-fired power stations. In Hydrocarbon Processing, 1999, p. 61 ff., S. M. Wilhelm gives an overview of methods of removing mercury from liquid hydrocarbon streams. An overview of the removal of mercury in olefin plants is given by Steve Coleman et al.: Feedstock Contaminants in Ethylene Plants, 2005 Spring National Meeting Atlanta, Ga., Apr. 10-14, 2005.

[0004] If metallic mercury is present in liquid form in streams of materials, the mercury is frequently removed by mechanical measures which exploit the high surface tension or the high specific gravity of mercury by decantation, by means of coalescence filters, activated carbon coated filters or the like. EP-A 0 761 830 discloses a simple, purely mechanical method in which finely divided mercury is collected by coalescence to form larger droplets of mercury which are easy to separate off. WO 2004/048624 describes a method of removing mercury by filtration through electrographite.

[0005] The removal of mercury is often also carried out using methods in which the mercury is bound to an adsorbent. Thus, DE-A 26 43 478 describes the separation of mercury from liquids by adsorption on activated carbon having a specific surface area of at least 250 m²/g. Carbon-based adsorbents are used, inter alia, for the removal of mercury from streams of materials, as described in U.S. Pat. No. 3,755,989. U.S. Pat. No. 4,500,327 describes sulfur-impregnated activated carbon for removing mercury from gaseous streams, while JP 52-53793 describes the use of iodide-comprising activated carbon for removing mercury from liquid streams. U.S. Pat. No. 4,909,926 and U.S. Pat. No. 4,094,777 describe the use of active compositions comprising CuS or CuO or Ag₂S on support materials such as aluminum oxide for removing mercury from streams of materials. EP-A 0 385 742

describes a process for removing mercury from liquid hydrocarbon streams comprising hydrocarbons having up to 8 carbon atoms by bringing the streams into contact with metallic copper or copper compounds present on a support.

[0006] The formation of solid amalgams is also often used for the removal of mercury. The most suitable metals for this purpose are the metals of group XI of the Periodic Table (Cu, Ag, Au), which are usually used in the form of an absorption composition in which the metal is finely distributed on a support. Thus, DE-A 21 02 039 discloses a process for removing mercury from gases, in which the mercury-comprising gases are brought into contact with a composition comprising copper on a porous aluminum oxide support. U.S. Pat. No. 4,230,486 discloses a process for removing mercury from liquids by passing the liquids over an absorbent comprising metallic silver on a porous support such as activated carbon or a ceramic support. DE-A 42 21 207 teaches a process for removing mercury from alkaline metal hydroxide solution or alkaline metal alkoxide solution by passing the solutions over silver-coated fibers. DE-A 41 16 890 discloses absorbents for removing mercury, which comprise, in particular, Cu, Ag, Fe and Bi, or else Au, Sn, Zn and Pd and also mixtures of the metals mentioned in metallic or oxidic or sulfidic form on an activated carbon support having a BET surface area of from 300 to 1000 m²/g.

[0007] U.S. Pat. No. 4,911,825 describes the removal of mercury and arsenic from hydrocarbon streams by bringing these into contact with a catalyst comprising nickel and palladium on aluminum oxide in the presence of hydrogen in a first step and into contact with an absorbent comprising sulfur or a metal sulfide, preferably copper sulfide or a combination of copper sulfide and silver sulfide, on a support in a second step. The process can also be carried out in a single stage over a mixture of the catalyst and the absorbent. FR-A 2 310 795 describes the removal of mercury from a gaseous natural gas stream using an absorbent comprising metallic gold, silver, copper or nickel on a support composed of silicon dioxide, aluminum oxide or an aluminosilicate having a BET surface area of from 40 to 250 m²/g. WO 91/15559 discloses a method of removing mercury from liquid hydrocarbon streams by bringing them into contact with an absorbent produced by mixing of a pulverulent oxide, preferably an oxide selected from among nickel oxide, copper oxide and cobalt oxide, with a porous support material such as aluminum oxide, silicon dioxide, zeolites or clays and subsequent reduction.

[0008] It is an object of the invention to provide an improved method of removing mercury from a mercury-comprising hydrocarbon stream.

[0009] This object is achieved by a method of removing mercury from a mercury-comprising hydrocarbon stream, in which the hydrocarbon stream is brought into contact with an absorbent comprising copper on a porous oxidic support material, wherein the hydrocarbon stream is brought into contact with the absorbent in the presence of hydrogen.

[0010] It has been found that a very much better removal of mercury from the hydrocarbon streams is achieved in the presence of hydrogen using copper-comprising absorbents which comprise copper on a support and are effective as hydrogenation catalysts than in the absence of hydrogen.

[0011] The absorbent used according to the invention comprises copper, preferably in reduced form, on a porous support material. The absorbent used according to the invention is effective as hydrogenation catalyst. Suitable porous sup-

port materials are amorphous and crystalline aluminosilicates, aluminum oxide, silicon dioxide, clays and metal oxides. Suitable clays are, for example, attapulgite, kaolin, bentonite, Fuller's earth. Suitable metal oxides are, for example, aluminum oxides and silicon dioxide and also magnesium oxide, zirconium dioxide, titanium dioxide, zinc oxide, chromium(III) oxide, barium oxide and mixtures thereof. A preferred aluminum oxide is γ -aluminum oxide.

[0012] It is possible to use all customary copper-comprising hydrogenation catalysts in activated (reduced) form in the method of the invention.

[0013] The copper comprising hydrogenation-active absorbents used according to the invention can be obtained by mixing of copper oxide with a support material and subsequent conversion of copper into the metallic form by reduction, preferably in a stream of hydrogen. The absorbents used according to the invention can also be produced by impregnation of the support material with an aqueous solution of a copper salt, drying, if appropriate calcination and conversion of the copper into the metallic form by reduction, preferably by means of a hydrogen-comprising gas stream, although it is also possible to use a reducing agent such as hydrazine.

[0014] In the absorbent used according to the invention, copper is generally present in reduced, i.e. metallic (elemental), form finely dispersed on the support material. In general, the absorbents used according to the invention comprise from 10 to 50% by weight of copper on an oxidic support material. Examples of suitable compositions on the basis of which the absorbents used according to the invention are obtained are compositions comprising copper oxide, zinc oxide and aluminum oxide or compositions comprising copper oxide, magnesium oxide, barium oxide, chromium(III) oxide, zinc oxide and silicon dioxide. Particular preference is given to a mixture of from 10 to 60% by weight of copper oxide, from 0 to 40% by weight of zinc oxide, from 0 to 20% by weight of aluminum oxide, from 5 to 25% by weight of magnesium oxide, from 10 to 40% by weight of silicon dioxide, from 0 to 5% by weight of chromium(III) oxide and from 0 to 10% by weight of barium oxide.

[0015] Hydrocarbon streams from which mercury can be removed according to the invention are any hydrocarbon streams which can be contaminated with mercury. These generally comprise aliphatic, aromatic, alicyclic and/or heterocyclic hydrocarbons having from 1 to 14 carbon atoms. Examples of hydrocarbon mixtures which can be freed of mercury according to the invention are LNG (liquefied natural gas), LPG (liquefied petroleum gas), naphtha and kerosene. Examples of pure hydrocarbons which can be purified according to the invention are ethylene and propylene and also aliphatic hydrocarbons.

[0016] The mercury content of the hydrocarbons or hydrocarbon mixtures before carrying out the method of the invention can be up to 100 ppm, but is generally up to 1 ppm of Hg. Mercury is generally present in the form of organomercury compounds.

[0017] The method of the invention can be carried out in the suspension mode or the fixed-bed mode. If it is carried out in the fixed-bed mode, it can be carried out in the upflow or downflow mode. The hydrocarbons or hydrocarbon mixtures comprising mercury or arsenic can be used in gaseous or liquid form. The hydrocarbons or hydrocarbon mixtures are preferably used in liquid form. Hydrogen is introduced together with the gaseous or liquid hydrocarbon or hydrocarbon mixture into a suitable reaction vessel and passed, gen-

erally in cocurrent, over the particulate absorbent present in a fixed bed. This can be carried out in the upflow or downflow mode. However, hydrogen and hydrocarbon or hydrocarbon mixture can also be passed over the bed of absorbent in countercurrent. The absorbent can also be present in suspension in the hydrocarbon or hydrocarbon mixture. In general, the method is carried out at a temperature of from 30 to 250° C., preferably from 60 to 180° C., and a hydrogen pressure of from 1 to 20 bar. The pressure is preferably selected so that the hydrocarbon or the hydrocarbon mixture is present as a liquid. The amount of hydrogen introduced generally corresponds to a space velocity of from 10 to 650 standard l per kg of absorbent and hour.

[0018] After the absorbent is exhausted, it can be thermally regenerated by heating it in a stream of inert gas or a hydrogen-comprising gas stream, in general at temperatures of from 180 to 400° C., for example from 200 to 220° C., and condensing out vaporized mercury.

[0019] The invention is illustrated by the following examples.

EXAMPLES

Comparative Example 1

[0020] A solution of diphenylmercury (Ph_2Hg) in 500 ml of octane, corresponding to 350 ppm of Hg, was heated to 60° C. in a glass flask. 1.5 standard l/h of hydrogen were passed into this solution while stirring. 5 g of an unreduced hydrogenation catalyst comprising 40% by weight of CuO, 40% by weight of ZnO and 20% by weight of Al_2O_3 in the form of 3x5 mm pellets (absorbent A) were added to this solution. Samples were taken from the solution after 2 h and 24 h and the mercury content of the samples was determined. The results are shown in table 1.

Comparative Example 2

[0021] A solution of diphenylmercury in 500 ml of octane, corresponding to 350 ppm of mercury, was heated to 60° C. in a glass flask. 5 g of the catalyst comprising 40% by weight of CuO, 40% by weight of ZnO and 20% by weight of Al_2O_3 which had previously been reduced and activated by means of H_2 at 180° C. (absorbent B) in the form of 3x5 mm pellets were added to this solution. Hydrogen was not passed in. The solution was stirred. Samples were taken after 2 h and 24 h and their mercury content was determined. The results are shown in table 1.

Example 1

[0022] The procedure of comparative example 2 was repeated, but 1.5 standard l/h of hydrogen were passed in. Samples were taken at regular intervals and their mercury content was determined. The results are shown in table 1.

Example 2

[0023] The procedure of example 1 was repeated, but the reduced catalyst was added in pulverulent form (absorbent C). Samples were taken at regular intervals and their mercury content was determined. The results are shown in table 1.

TABLE 1

Time [h]	Comp. Ex. 1 Hg [ppm]	Comp. Ex. 2 Hg [ppm]	Example 1 Hg [ppm]	Example 2 Hg [ppm]
0	350	350	350	350
1	—	270	250	205
2	310	—	150	115
3	—	—	120	75
4	—	—	—	60
5	—	—	72	45
6	—	145	51	15
7	—	—	37	—
8	—	—	28	—
21	—	—	—	0.3
22	—	—	—	0.3
24	135	47	0.8	0.3

Example 3

[0024] The procedure of example 1 was repeated, but the solution was maintained at 25° C. Samples were taken at regular intervals and their mercury content was determined. The results are shown in table 2.

Example 4

[0025] The procedure of example 1 was repeated. The temperature was thus 60° C. Samples were taken at regular intervals and their mercury content was determined. The results are shown in table 2.

Example 5

[0026] The procedure of example 1 was repeated, but the solution was heated to 100° C. Samples were taken at regular intervals and their mercury content was determined. The results are shown in table 2.

TABLE 2

Time [h]	Example 3 (25° C.) Hg [ppm]	Example 4 (60° C.) Hg [ppm]	Example 5 (100° C.) Hg [ppm]
0	350	350	350
1	300	250	90
2	290	150	—
3	250	120	30
4	240	—	—
5	220	72	—
6	205	51	2.3
7	—	37	—
8	—	28	—
22	80	—	—
24	75	0.8	0.14
93	4.6	—	—

Example 6

[0027] The experiments were carried out in a monoline reactor having an internal diameter of 6 mm and a total length of 5 m. The reactor comprised 4 segments connected to one another by means of a capillary. The reactor was operated in the downflow mode. The reactor segments were maintained at 60° C. The liquid hydrocarbon feed was mixed with hydrogen before the reactor inlet. The reactor output was cooled by means of a low-temperature condenser and the gas phase was separated from the liquid phase. The liquid phase was employed for determining the mercury content and the gas phase was disposed of via a mercury guard bed.

[0028] 80 g of a catalyst comprising 45% by weight of CuO, 16% by weight of MgO, 35% by weight of SiO₂, 0.9% by weight of Cr₂O₃, 1.1% by weight of BaO and 0.6% by weight of ZnO in the form of 3×5 mm pellets were present in the reactor. A glass sphere having a diameter of 2 mm was present between each of the individual pellets. The catalyst was firstly activated in a stream of hydrogen at from 180 to 220° C. The reactor was subsequently cooled to 60° C. in a stream of hydrogen. The reactor was operated at atmospheric pressure.

[0029] Octane which had been saturated over an organomercury compound was used as feed. In part of the experiments, phenylmercury acetate PhHgOAc was used as organomercury compound, and in another part of the experiments mercury acetate Hg(OAc)₂ was used as organomercury compound. A number of batches having different mercury concentrations were used in each case. 100 standard l/h of the mercury-comprising octane and 2 standard l/h of hydrogen were metered in. The results of the experiments are summarized in table 3.

TABLE 3

Experiment No.	Hg compound added	Hg concentration in the feed [ppm]	Hg concentration in the output [ppm]
1	PhHgOAc	80	0.004
2	PhHgOAc	90	0.002
3	PhHgOAc	80	0.004
4	PhHgOAc	60	0.001
5	Hg(OAc) ₂	6	0.001
6	Hg(OAc) ₂	1.4	0.001
7	Hg(OAc) ₂	0.6	0.001
8	Hg(OAc) ₂	2.8	0.001
9	Hg(OAc) ₂	1.2	0.001
10	PhHgOAc	90	0.001
11	PhHgOAc	120	0.003
12	PhHgOAc	75	0.004

1.-8. (canceled)

9. A method of removing mercury from a mercury-comprising hydrocarbon stream, which comprises bringing a hydrocarbon stream into contact with an absorbent comprising copper on a support material, wherein the hydrocarbon stream is brought into contact with the absorbent in the presence of hydrogen, wherein the absorbent comprises from 10 to 60% by weight of copper oxide, from 0 to 40% by weight of zinc oxide, from 0 to 20% by weight of aluminum oxide, from 5 to 25% by weight of magnesium oxide, from 10 to 40% by weight of silicon dioxide, from 0 to 5% by weight of chromium(III) oxide and from 0 to 10% by weight of barium oxide.

10. The method according to claim 9, wherein copper is present on a porous oxidic support material.

11. The method according to claim 9, wherein the absorbent comprises from 10 to 60% by weight of copper.

12. The method according to claim 9, wherein the hydrocarbon stream is present in liquid form.

13. The method according to claim 9, wherein the absorbent is present as a fixed bed.

14. The method according to claim 13, wherein the hydrocarbon stream is brought into contact with the absorbent in the upflow mode or the downflow mode.

15. The method according to claim 12, wherein the absorbent is present in suspension in the hydrocarbon stream.

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