b1) increasing the reaction temperature to a temperature T2 and preparing the alkyl mercaptan at the temperature T2 for a time period t2, followed by

b2) decreasing the reaction temperature from a temperature T2 to a temperature T3 and preparing the alkyl mercaptan at the temperature T3 for a time period t3,

wherein

the temperature T2 is always higher than the temperatures T1 and T3,

n is an integer larger than zero,

and

an aluminum oxide-based catalyst containing an alkali tungstate is used.

According to the process of the present invention at least one temperature cycle is performed, where the reaction temperature is increased in step b1) to a temperature T2 and in step b2) the temperature T2 is decreased to a temperature T3. When several temperature cycles are performed, the term reaction temperatures refers to the temperature T1 as the starting reaction temperature for the first reaction cycle and to the temperature T3 as the starting reaction temperature for the second and any further temperature cycles.

Typically, the synthesis of alkyl mercaptans from an aliphatic alcohol and hydrogen sulfide is performed at temperatures of from ca. 250°C to ca. 500°C. Further, said synthesis is typically performed at pressures of from 1 bar to ca. 50 bar. In the context of the present invention the term ca. is used with respect to temperatures to denote all conceivable temperatures which differ by +/- 10°C from the explicitly mentioned temperature. Thus, the term ca. 250°C comprises all integral and real number values for temperatures of from 240°C to 260°C, in particular the integral values 240°C, 241°C, 242°C, 243°C, 244°C, 245°C, 246°C, 247°C, 248°, 249°C, 250°C, 251°C, 252°C, 253°C, 254°C, 255°C, 256°C, 257°C, 258°C, 259°C and 260°C. Correspondingly, the term ca. 500°C comprises all integral and real number values for temperatures of from 490°C to 510°C, in particular the integral values 490°C, 491°C, 492°C, 493°C, 494°C, 495°C, 496°C, 497°C, 498°C, 499°C, 500°C, 501°C, 502°C, 503°C, 505°C, 506°C, 507°C, 508°C, 509°C and 510°C. Further, in the context of the present invention the term ca. is used with respect to pressures to denote all conceivable pressures which differ by +/- 5 bar from the explicitly mentioned pressure. Thus, the term ca. 50 bar comprises all integral and real number values for pressures of from 45 bar to 55 bar, in particular the integral values 45 bar, 46 bar, 47 bar, 48 bar, 49 bar, 50 bar, 51 bar, 52 bar, 53 bar, 54 bar and 55 bar.

Typically, the temperature T1, also referred to as the initial temperature T1, and the temperature T3 in step b2) in the process according to the present invention independently from each other range from ca. 250°C to ca. 350°C because the use of temperatures in this range already allows the synthesis of alkyl mercaptans with a selectivity of ca. 95%. The thus obtained alkyl mercaptan selectivity is essentially constant over several days or even several weeks. The term ca. 250°C is used according to the aforementioned understanding of this term in context of the present

b) performing temperature cycle of the number n, comprising the steps of

b1) increasing the reaction temperature to a temperature T2 and preparing the alkyl mercaptan at the temperature T2 for a time period t2, wherein at least 95 %, preferably more than 95 % or 97 % and more preferably to 99 % or even 100% of the aliphatic alcohol fed into the reaction is converted, followed by

b2) decreasing the reaction temperature from the temperature T2 to a temperature T3 and preparing the alkyl mercaptan at the temperature T3 for a time period t3, wherein 95 % at the most, preferably less than 95 % or 92 % of the aliphatic alcohol fed into the reaction is converted,

wherein

the temperature T2 is always higher than the temperatures T1 and T3,

n is an integer larger than zero,

and

an aluminum oxide-based catalyst containing an alkali tungstate is used.

Regarding the temperature T2 in different temperature cycles, the process according to the present invention is not subject to any other limitations than that the temperature T2 is always higher than the temperatures T1 and T3. It is for example possible that the temperature T2 has the same value in each temperature cycle. In this case, the temperature T2 in a temperature cycle of the number n has the same value as the temperature T2 in the preceding temperature cycle of the number n-1. This scenario is suitable for situations, where one and the same value of the temperature T2 typically leads to the same increase of selectivity for the formation of the respective alkyl mercaptan.

Therefore, in one embodiment of the process according to the present invention the temperature T2 in a temperature cycle of the number n has the same value as the temperature T2 in the preceding temperature cycle of the number n-1.

Alternatively, it is also possible to increase the temperature T2 in every consecutive temperature cycle by a specific temperature range, e.g. by a temperature range of 1°C, 2°C, 3°C, 4°C or 5°C relative to the temperature T2 in the preceding temperature cycle. For example, after the fifth temperature cycle (temperature cycle of the number n = 5) with a temperature T2 = 350°C was performed, the temperature T2 is increased to a value of e.g. 351°C, 352°C, 353°C, 345°C or 345°C in the next temperature cycle 6 (temperature cycle of the number n = 6, i.e. temperature cycle n + 1, relative to the preceding temperature cycle). This scenario is suitable for situations, where one and the same value for the temperature T2 does no longer give the same increase of selectivity for the formation of the respective alkyl mercaptan. It is believed that in cases like this only a steady increase of the temperature T2 in a consecutive temperature cycle can again lead

tetratungstate ($Cs_8W_4O_{16}$), cesium heptatungstate ($Cs_6W_7O_{24}$), cesium decatungstate ($Cs_4W_{10}O_{32}$) or cesium dodecatungstate ($Cs_2W_{12}O_{40}$).

Suitable promoters are also alkali metal tungstates with a molar ratio of alkali metal to tungsten of less than 2:1, for example alkali metal tungsten bronzes. Preferably, the alkali metal tungsten bronze is an oxidic composition which corresponds to the general formula A_xWO_y, wherein A is at least one alkali metal selected from the group consisting of sodium, potassium, cesium, rubidium and mixtures thereof, x is equal to or larger than 0.9 and smaller than 2, i.e. x corresponds to the condition $0.9 \leq x < 2$, and y is equal to or larger than 3.4 and smaller than 4, i.e. y corresponds to the condition $3.4 \leq y < 4$. The molar ratio of an alkali metal to tungsten preferably ranges from less than 2:1 to 0.9:1, especially from 1.9:1 to 1:1. The alkali metal tungsten bronzes $K_{1.6}WO_y$, $Rb_{0.9}WO_y$, $K_{0.7}WO_y$ and $Na_{0.3}Cs_{1.1}WO_y$ are particularly suitable promoters for catalysts in the preparation of alkyl mercaptans.

It was found that the process and in particular the temperature cycles according to the present invention give particularly good results when a catalyst is used which contains a cesium tungstate.

Thus, in one embodiment of the process according to the present invention the catalyst contains a cesium tungstate.

In addition to the alkali metal tungstate, catalysts for the alkyl mercaptan production can also contain a halide, which is selected from the group consisting of fluoride, chloride, bromide, iodide and mixtures thereof. The additional presence of the halide does not affect the molar ratio of the at least one alkali metal to tungsten. Preferably, the halide containing alkali metal tungsten promoter therefore corresponds to the general formula $A_xWO_yX_z$, wherein A is at least one alkali metal selected from the group consisting of sodium, potassium, cesium, rubidium and mixtures thereof, x is equal to or larger than 0.9 and smaller than 2, i.e. x corresponds to the condition $0.9 \leq x < 2$, W is tungsten, y is equal to or larger than 3.4 and smaller than 4, i.e. y correspond to the condition $3.4 \leq y < 4$, X is at least one halide selected from the group consisting of fluoride, chloride, bromide, iodide and mixtures thereof, and z is equal to or larger than 0.01 and smaller than 12, i.e. z corresponds to the condition $0.01 \leq z < 12$. A suitable halide containing promoter is for example Cs_2WO_4 with added cesium fluoride, cesium chloride, cesium bromide, cesium iodide or combination thereof, in particular the combination of cesium fluoride and cesium bromide.

The common processes for the preparation of catalysts, which are suitable for the production of alkyl mercaptans, provide said catalysts in their oxidic form, which however is considered the inactive or inert form of these catalysts. Activation of said catalysts is usually caused by the

Patent claims

1. Process for the preparation of an alkyl mercaptan by reacting an aliphatic alcohol with hydrogen sulfide in the presence of a heterogeneous catalyst comprising the steps of

a) starting the preparation of an alkyl mercaptan at a temperature T1 and preparing the alkyl mercaptan at the temperature T1 for a time period t1, and

b) performing temperature cycles of the number n, comprising the steps of

b1) increasing the reaction temperature to a temperature T2 and preparing the alkyl mercaptan at the temperature T2 for a time period t2, followed by

b2) decreasing the reaction temperature from the temperature T2 to a temperature T3 and preparing the alkyl mercaptan at the temperature T3 for a time period t3,

wherein

the temperature T2 is always higher than the temperatures T1 and T3,
n is an integer larger than zero,

and

an aluminum oxide-based catalyst containing an alkali tungstate is used.

2. Process according to claim 1, wherein the temperature T1 and the temperature T3 independently from each other range from 250°C +/- 10°C to 350°C +/- 10°C.

3. Process according to claim 1 or 2, wherein the temperature T2 is at least 5°C higher than each of the temperatures T1 and T3.

4. Process according to any of claims 1 to 3, wherein the temperature T3 of a temperature cycle of the number n has an equal or a different value compared to the temperature T3 in the preceding temperature cycle of the number n-1.

5. Process according to any of claims 1 to 4, wherein the temperature T2 in a temperature cycle of the number n has the same value as the temperature T2 in the preceding temperature cycle of the number n-1.

6. Process according to any of claims 1 to 4, wherein the temperature T2 in a temperature cycle of the number n has a higher value than the temperature T2 in the preceding temperature cycle of the number n-1.

7. Process according to any of claims 1 to 6, wherein the time period t1 ranges from 1 hour +/- 10% to a month.

8. Process according to claim 7, wherein the time period t2 ranges from 1 hour +/- 10% to 50 hours +/- 10%.

9. Process according to any of claims 1 to 8, wherein the time period t3 is until the recharging of the reactor with a new catalyst.

10. Process according to claim 9, wherein the time period t3 is up to a month.

11. Process according to any of claims 1 to 10, wherein the catalyst contains a cesium tungstate.

12. Process according to any of claims 1 to 11, wherein the catalyst is sulfidized prior to its use in the preparation of alkyl mercaptans.

13. Process according to any of claims 1 to 12, wherein the aliphatic alcohol is a C_1-C_3 alcohol.

14. Process according to claim 13, wherein the aliphatic alcohol is methanol, ethanol, n-propanol, iso-propanol or tert-butanol.

15. Process according to claim 14, wherein the aliphatic alcohol is methanol.