DESCRIPTION

TITLE: Process for preparing a compound of formula RSH by hydrosulfurization

Summary

In one aspect, the present disclosure refers to a method for preparing a compound of formula RSH where R represents an alkyl group, by gas-phase catalytic reaction of hydrogen sulfide with a compound of formula ROH, in the presence of a solid catalyst, characterized in that the reaction is performed in the presence of a catalyst which comprises or consists of one or several pure or mixed rare-earth oxide(s), ~~one or several pure or mixed rare-earth sulfide(s), or one or several pure or mixed rare-earth oxysulfide(s),~~ provided that when the rare earth is lanthanum, said catalyst is a mixed oxide of lanthanum and of at least one metal selected from rare earths and one metal ~~or~~ which is not selected from rare earths, and when the rare earth is cerium, said catalyst is supported on alumina.

Detailed Description

The invention concerns a method for gas-phase catalytic hydrosulfurization of an alcohol into the corresponding thiol. More particularly, it is described for the production of methanethiol from methanol and hydrogen sulfide, without its scope being restricted thereto.

The hydrosulfurization reaction of methanol into methanethiol through a gas-phase catalytic route is known. Usually, this is carried out in the presence of a catalyst based on an oxide of tungsten and of an alkaline metal supported on an alumina, as described for example in the patent WO2013092129A1.

Nevertheless, there are some researches covering alternative catalysts in the literature. Thus, the works of Plaisance and Dooley (Catalysis Letters, 2009, 128, 449-458) describe the use of catalysts based on different oxides of metals such as tungsten (WO_3), lanthanum (La_2O_3) or titanium (TiO_2) supported on various solids. Amongst all of these, tungsten oxide is most active one. These works highlight the fact that the activity of each of the tested catalysts depends on different parameters and that it is hard to determine optimum conditions that are common to several catalysts. In addition, with the catalyst based on lanthanum oxide supported on alumina (La_2O_3/Al_2O_3), a high methanol conversion is obtained, but this is accompanied with a very low methanethiol selectivity, which makes this catalyst incompatible with an application on an industrial scale.

CLAIMS

1. A method for preparing a compound of formula RSH where R represents an alkyl group, by gas-phase catalytic reaction of hydrogen sulfide with a compound of formula ROH, in the presence of a solid catalyst, characterized in that the reaction is performed in the presence of a catalyst which comprises or consists of one or several pure or mixed rare-earth oxide(s), ~~one or several pure or mixed rare-earth sulfide(s), or one or several pure or mixed rare-earth oxysulfide(s),~~ provided that when the rare earth is lanthanum, said catalyst is a mixed oxide of lanthanum and of at least one metal selected from rare earths and one metal ~~or~~ which is not selected from rare earths, and when the rare earth is cerium, said catalyst is supported on alumina.

~~2. The preparation method according to claim 1, characterized in that the catalyst is selected from one or several mixed oxide(s) of several rare earths, one or several mixed oxide(s) of one or several rare earth(s) and of at least one other metal that is not a rare earth, one or several mixed sulfide(s) of several rare earths, one or several mixed sulfide(s) of one or several rare earth(s) and of at least one other metal that is not a rare earth, one or several oxysulfide(s) of several rare earths, one or several mixed oxysulfide(s) of one or several rare earth(s) and of at least one other metal that is not a rare earth, and mixtures of said mixed oxides, mixed sulfides and mixed oxysulfides.~~

~~3.~~2. The preparation method according to claim 1 ~~or 2~~, characterized in that said metal that is not a rare earth is zirconium.

~~4.~~3. The preparation method according to ~~any one of~~ claim~~s~~ 1 ~~to 3~~or 2, characterized in that the catalyst comprises one or several oxide(s) of metals other than rare earths.

~~5.~~4. The preparation method according to any one of claims 1 to ~~4~~3, characterized in that the catalyst is supported.

~~6.~~5. The preparation method according to any one of claims 1 to ~~5~~4, characterized in that the catalyst is supported on alumina, whether pretreated or not.

~~7.~~6. The preparation method according to any one of claims 1 to ~~6~~5, characterized in that ~~the methanethiol~~ RSH wherein R is methyl is prepared by catalytic hydrosulfurization of methanol in a gas phase by reaction with hydrogen sulfide.

~~8.~~7. The preparation method according to any one of claims 1 to ~~7~~6, characterized in that the catalyst comprises or consists of mixed oxides of lanthanum, cerium, neodymium and zirconium, the proportions of zirconium and cerium oxides being predominant.

~~9.~~8. The preparation method according to any one of claims 1 to ~~7~~7, characterized in that the catalyst comprises or consists of cerium oxide and is supported within ranges comprised between 0.1% and 50% (m/m), preferably between 0.5% and 30%, on an alumina impregnated with potassium whose content is comprised between 0.1% and 20% (m/m), preferably between 0.5% and 10%, and more preferably between 0.5% and 5%.

~~10.~~9. The preparation method according to any one of claims 1 to ~~9~~8, characterized in that the molar ratio between the hydrogen sulfide and the compound ROH is comprised between 0.5 and 20, preferably from 1 to 15, and more preferably from 1 to 10.

~~11.~~10. The preparation method according to any one of claims 1 to ~~10~~9, characterized in that the reaction is performed at a temperature comprised between 200°C and 450°C, preferably from 250°C to 420°C, and more preferably from 275°C to 400°C, advantageously under a pressure comprised between 2 and 20 bar, preferably from 5 to 15 bar, and more preferably from 7 to 14 bar, and the contact time of the compound ROH with the catalyst is comprised between 0.1 second and 60 seconds.

~~12.~~11. The preparation method according to any one of claims 1 to ~~11~~10, characterized in that the reaction produces dimethyl sulfide and in that a catalytic conversion reaction of said dimethyl sulfide into methanethiol is further performed.