Sulfhydrolysis reaction

$$RSR' + H_2S \rightarrow RSH + R'SH \quad (5)$$

In the case of methyl mercaptan, the sulfhydrolysis reaction is written according to equation (6) below:

$$CH_3SCH_3 + H_2S \rightarrow 2\ CH_3SH \quad (6)$$

The sulfhydrolysis reaction is generally catalyzed with catalysts of alumina type (Al_2O_3) or of NiMo (nickel/molybdenum) or CoMo (cobalt/molybdenum) type on an alumina support, as described in patent applications WO 2017/210070 and WO 2018/035316.

Patents US 4 396 778 and US 4 313 006 describe the use of zeolites as catalysts for the sulfhydrolysis reaction. However, the zeolites described are used directly and are not pretreated. Furthermore, the operating conditions of the tests performed are not suitable for industrial production (notably with low productivities).

Such a sulfhydrolysis process thus needs to be improved so as to be more efficient and more suited to the industrial scale.

There is thus a need for an improved process for the sulfhydrolysis of dialkyl sulfides to mercaptans, in particular of dimethyl sulfide to methyl mercaptan.

There is also a need for an improved process for upgrading dialkyl sulfides, in particular dimethyl sulfide, which are generated as byproducts during the production of mercaptans produced from alcohol(s) and hydrogen sulfide.

One objective of the present disclosure is to propose a process for the sulfhydrolysis of dialkyl sulfides to mercaptans which is efficient and easy to perform industrially, notably with an improved catalyst.

Another objective of the present disclosure is to propose a process for the sulfhydrolysis of dialkyl sulfides to mercaptans which can be readily integrated into a unit for the industrial production of mercaptans, notably produced from alcohol(s) and H_2S.

One objective of the present disclosure is to provide an integrated process for preparing mercaptans in which the dialkyl sulfides generated as byproducts (for example during the reaction between an alcohol and H_2S) are recycled or economically upgraded in a manner that is industrially viable, easy and safe for the operators.

The present inventors have discovered, surprisingly, that pretreatment of the catalysts used for sulfhydrolysis allows improved conversion of dialkyl sulfides while at the same time maintaining high selectivity of the reaction for mercaptans. The yield and productivity of the process are thus improved. In particular, the dialkyl sulfide conversion is improved relative to the conversion obtained in the presence of the same untreated catalyst. An increase in

conversion of at least 8%, or even at least 10%, is notably obtained by means of the pretreatment of the catalyst according to the idisclosure.

The sulfhydrolysis process thus improved may be integrated into a plant for the industrial production of mercaptans, notably produced from at least one alcohol and H_2S (main reaction). The sulfhydrolysis process according to the disclosure then makes it possible to increase the mercaptan productivity in a simple and economical manner by upgrading the dialkyl sulfides generated as byproducts during the main reaction and transforming them also into mercaptans.

Furthermore, the mercaptans derived from the sulfhydrolysis and the unreacted H_2S can be reintroduced directly (notably without an intermediate purification step) into the main reactor, and without this having any consequence on the reaction between the alcohol(s) and the H_2S. The mercaptans produced by the two reactions (main reaction and sulfhydrolysis reaction) can then be purified and/or recovered in a single place, for example at the outlet of the main reactor. This integration of the sulfhydrolysis process into the main mercaptan production chain can be reinforced by the presence of a single H_2S feed for both the main reaction and the sulfhydrolysis reaction (for example at the inlet of the sulfhydrolysis reactor).

Thus, according to the disclosure, a simple and efficient process for the upgrading of dialkyl sulfides which is totally integrated into an industrial mercaptan production chain may be obtained. This device is notably easy to implement: it can be readily connected to the main unit and requires only minimal modifications thereof.

Thus, the present disclosure relates to a process for preparing at least one mercaptan, comprising the following steps:

i) treatment of a catalyst for the sulfhydrolysis of at least one dialkyl sulfide, preferably a zeolite, said treatment comprising the following steps:

1) heating said catalyst, preferably in the presence of an inert gas; and

2) placing said catalyst in contact with hydrogen sulfide (H_2S); and then

ii) a sulfhydrolysis reaction in which at least one dialkyl sulfide is reacted with H_2S in the presence of said catalyst treated according to step i), to obtain at least one mercaptan.

The present invention also relates to a process for preparing at least one mercaptan, preferably continuously, comprising the following steps:

A) H_2S and at least one alcohol are introduced into a first reactor;

B) the H_2S and said at least one alcohol are reacted to obtain an outlet stream comprising at least one mercaptan and at least one dialkyl sulfide and possibly H_2S;

C) the outlet stream obtained from step B) is separated into:

- a stream F1 comprising the mercaptan(s),
- a stream F2 comprising the dialkyl sulfide(s), and

- optionally a stream F3 comprising H_2S;

D) optionally, the stream F2 is purified to obtain a stream F2' enriched in dialkyl sulfide(s);

E) stream F2 or F2' and H_2S are introduced into a second reactor, said reactor comprising a catalyst treated according to the treatment process as defined above;

F) a sulfhydrolysis reaction of the dialkyl sulfide(s) with H_2S is performed to obtain an outlet stream F4 comprising said mercaptan(s) and possibly H_2S;

G) optionally, stream F4 obtained from step F) is recycled into step A).

In an aspect, there is provided a process for preparing at least one mercaptan, comprising the following steps:

i) treatment of a catalyst for the sulfhydrolysis of at least one dialkyl sulfide, comprising the following steps:

1) heating said catalyst, preferably in the presence of an inert gas; and

2) placing said catalyst in contact with hydrogen sulfide (H_2S); and then

ii) a sulfhydrolysis reaction in which at least one dialkyl sulfide is reacted with H_2S in the presence of said catalyst treated according to step i), to obtain at least one mercaptan;

said catalyst being a zeolite.

In another aspect, there is provided a process for preparing at least one mercaptan, preferably continuously, comprising the following steps:

A) H_2S and at least one alcohol are introduced into a first reactor;

B) the H_2S and said at least one alcohol are reacted to obtain an outlet stream comprising at least one mercaptan and at least one dialkyl sulfide and possibly H_2S;

C) the stream comprising at least one mercaptan, at least one dialkyl sulfide and possibly H_2S is separated into:

- a stream F1 comprising the mercaptan(s),
- a stream F2 comprising the dialkyl sulfide(s), and
- optionally a stream F3 comprising H_2S;

D) optionally, stream F2 is purified to obtain a stream F2' enriched in dialkyl sulfide(s);

E) stream F2 or F2' is introduced with H_2S into a second reactor, said reactor comprising a catalyst treated according to the treatment of step i) as defined above;

F) a sulfhydrolysis reaction of the dialkyl sulfide(s) with H_2S is performed to obtain an outlet stream F4 comprising said mercaptan(s) and possibly H_2S;

G) optionally, stream F4 obtained from step F) is recycled into step A).

Definitions

The term "*catalyst*" notably means a substance or a composition of chemical substances which accelerate a chemical reaction and which are found unchanged at the end of this reaction.

The usual definitions of conversion and selectivity are as follows:

Conversion% = (number of moles of reagent in the initial state – number of moles of reagent in the final state) / (number of moles of reagent in the initial state) × 100

Mercaptan selectivity = Number of moles of reagent converted into the desired product / X * (number of moles of reagent in the initial state – number of moles of reagent in the final state) × 100

with X = 2 if the dialkyl sulfide is symmetrical or X = 1 if the dialkyl sulfide is dissymmetrical.

The term "GHSV" (Gas Hourly Space Velocity), expressed in h^{-1}, is notably understood as follows:

[Math 1]

$$GHSV = \frac{Q \,.\, T \,.\, P^0}{V_{cat} \,.\, P \,.\, 273,15}$$

with:

Q = inlet gas flow rate in NL/h (normo liters per hour)

T = reaction temperature in Kelvins

P^0 = standard pressure in bar

P = reaction pressure in bar

V_{cat} = catalyst volume (L).

In particular, pretreatment of the catalysts according to the invention make it possible to obtain a dialkyl sulfide conversion of between 30% and 90%, preferably between 40% and 80% and even more preferentially between 40% and 75%.

The selectivity of the sulfhydrolysis reaction for mercaptans is notably greater than or equal to 99%, or even greater than 99.5%.

Hereinbelow, it is understood that when two reagents are introduced into a reactor, they may each be introduced separately into the reactor or may be combined before being introduced into the reactor.