

RTMP

PROCESS FOR THE PREPARATION OF METHYL MERCAPTAN

The present invention relates to an improved process for the preparation of methyl mercaptan. The invention relates more particularly to a process for the preparation of methyl mercaptan from methanol and hydrogen sulphide. The invention also relates to catalysts which are useful in this preparation and which have improved stability.

The preparation of methyl mercaptan from methanol and hydrogen sulphide has been known for some considerable time. A description of this type of reaction is given, for example, by Sabatier and Mailhe in 1910 in a Science Academy Report 150 823-6, 1569-72 and 1217-21.

The reaction is described as taking place in the presence of various catalysts based especially on alumina optionally doped with various metals, among which mention may be made of alkali metals, alkaline-earth metals, cadmium sulphide, antimony sulphide, tin oxide, phosphotungstic acid, phosphomolybdic acid and potassium tungstate.

The reaction proceeds in a single reactor or in several successive reactors. Thus, according to GB patent 1,417,532, it is known to prepare methyl mercaptan by reaction of methanol and hydrogen sulphide in a molar ratio of hydrogen sulphide to methanol of between 1.10:1 and 2.5:1, in a series of at least three

catalytic reactors. The catalyst employed is preferably an alumina doped with potassium tungstate, the reaction temperature being maintained between 320 and 370°C.

The reaction side products in this type of process consist essentially of dimethyl sulphide and carbon dioxide. The formation of dimethyl sulphide increases with the reaction temperature, but the degree of conversion of the methanol also increases with the temperature, and hence an equilibrium must be found between the formation of dimethyl sulphide and the conversion of the starting methanol.

It is also known from the articles of the Russian authors Kudenov, Paukshtis and Mashkina published in React. Kinet. Catal. Lett., Vol. 38, No. 1, 199-203 (1989) to use as reaction catalysts aluminas doped with potassium tungstate, with potassium carbonate, with potassium hydroxide or with sodium hydroxide, at temperatures of between 360 and 450°C. The best selectivity towards methyl mercaptan is obtained using potassium tungstate either at 360 or at 400°C. The best degree of methanol conversion is obtained when the temperature is highest, that is to say at 500°C. If the yield of methyl mercaptan is calculated as a function of the temperature and of the type of catalyst used, one would be inclined to use a temperature of between 400 and 450°C without distinction as regards the type of catalyst.

According to another article from the same

authors, published in Kinetika i Kataliz, Vol. 29, No. 5, pp. 1174-1180, September-October 1988 and which compares the activity and selectivity of alumina-based catalysts doped with potassium tungstate or with
5 potassium carbonate, it was observed that at a temperature of 360°C the selectivity towards methyl mercaptan was the same regardless of whether a catalyst doped with the tungstate or with the carbonate was used.

10 The present invention is based on the entirely surprising appreciation that the activity and selectivity towards methyl mercaptan of these two types of catalyst are quite different when they are used at lower temperatures than temperatures previously used in
15 the art.

 Accordingly, the present invention provides a process for the preparation of methyl mercaptan by reacting methanol and hydrogen sulphide in the vapour phase in the presence of a catalyst, wherein the
20 catalyst is an alkali metal carbonate deposited on alumina and wherein the reaction takes place at a temperature below 350°C.

 The alkali metal carbonate used is chosen from sodium, potassium and caesium carbonates.
25 Potassium carbonate is preferred. The amount by weight of alkali metal carbonate deposited on the alumina varies as a function of the nature of the alkali metal, but will generally be between 2 and 20 % by weight.

When potassium carbonate is used, the amount deposited on the alumina will preferably be between 2 and 10 % by weight, more preferably about 6.4 % by weight.

The reaction temperature is preferably
5 between 230 and 330°C and most preferably between 280 and 310°C. The reaction temperature is the temperature measured at the reactor inlet. The inlet temperature is generally below the outlet temperature, since the reaction is exothermic.

10 The reaction pressure is preferably between 8 and 15 bar (8 to 15 × 10⁵ pascals).

The catalyst is preferably distributed in a catalyst system comprising at least three reactors.

In a first reactor, also referred to as the
15 converter, preferably all of the hydrogen sulphide is introduced, the methanol being introduced sequentially into each of the other reactors. The overall molar ratio of hydrogen sulphide introduced to methanol introduced is between 1.5:1 and 2.5:1. The catalyst
20 used in the converter is preferably alumina. Its role is essentially to convert recycled dimethyl sulphide (originating from the last reactor), in the presence of fresh hydrogen sulphide, into methyl mercaptan.

At the converter outlet, the gases produced
25 are introduced into a reactor which is, at the same time, supplied with methanol, this methanol being introduced partly in liquid form and partly in gaseous form so as to stabilize the reactor temperature. The

reason for this is that vaporization of the methanol makes it possible to consume some of the heat produced by the exothermic reaction. The charge of methanol entering, methanol originating from the preceding reactor and fresh methanol introduced, is, in particular, increasingly large in each of the reactors as the reaction progresses. For each of the reactors, the molar ratio of the hydrogen sulphide to the partial supply of methanol gradually lowers as the reaction progresses and is, in particular, between 15:1 and 3:1.

The overall ratio of the hydrogen sulphide to the methanol is always within the limits previously indicated. These values make it possible to obtain a high selectivity towards methyl mercaptan to the detriment of the formation of dimethyl sulphide.

After the last reactor, the reaction mixture is introduced into a finisher containing the same catalyst as the preceding series of reactors, but in an equal or larger volume. At the finisher outlet, the reaction gases, consisting of methyl mercaptan, dimethyl sulphide, methanol and hydrogen sulphide and various gases, are separated according to the abovementioned GB patent 1,417,532.

The invention also relates to catalysts for the preparation of methyl mercaptan which are of improved stability relative to the potassium tungstate-based catalysts known in the prior art cited. This stability is improved over time.

The following examples illustrate the present invention.

EXAMPLE 1

Preparation of a catalyst of formula
5 K_2CO_3/Al_2O_3 at a concentration of 2 % by weight,
equivalent to an alkali metal cation number of
28.9 mmol/100 g of catalyst.

A 120 ml solution is prepared by dissolving
4.08 g of K_2CO_3 (sodium-free) in deionized water. The pH
10 of the final solution is 11.66. 200 g of Procalyse
Spheralite 505 alumina are dry-impregnated with the
above solution. The catalyst thus prepared is activated
at 470°C. The catalyst consists of 2 % by weight of
 K_2CO_3 .

15 EXAMPLE 2

Preparation of a catalyst of formula
 K_2CO_3/Al_2O_3 at a concentration of 6.4 % by weight,
equivalent to an alkali metal cation number of
92.6 mmol/100 g of catalyst.

20 The catalyst is prepared according to the
method described in Example 1, using 13.68 g of K_2CO_3 to
impregnate 200 g of alumina. The pH of the solution
before impregnation is 11.6.

EXAMPLE 3

25 Preparation of a catalyst of formula
 K_2CO_3/Al_2O_3 at a concentration of 10 % by weight,
equivalent to an alkali metal cation number of
144.7 mmol/100 g of catalyst.

The catalyst is prepared according to the method described in Example 1, using 22.22 g of K_2CO_3 to impregnate 200 g of alumina. The pH of the solution before impregnation is 11.75.

5 **EXAMPLE 4**

Preparation of a catalyst of formula Na_2CO_3/Al_2O_3 at a concentration of 4.9 % by weight, equivalent to an alkali metal cation number of 92.4 mmol/100 g of catalyst.

10 The catalyst is prepared according to the method described in Example 1, using 10 g of Na_2CO_3 to impregnate 200 g of alumina. The pH of the solution before impregnation is 10.79.

EXAMPLE 5

15 Preparation of a catalyst of formula Cs_2CO_3/Al_2O_3 at a concentration of 15.1 % by weight, equivalent to an alkali metal cation number of 92.5 mmol/100 g of catalyst.

20 The catalyst is prepared according to the method described in Example 1, using 35.49 g of Cs_2CO_3 to impregnate 200 g of alumina. The pH of the solution before impregnation is 11.02.

COMPARATIVE EXAMPLE 1

This catalyst consists of alumina alone.

25 The catalyst of Comparative Example 1 consists of non-impregnated Spheralite 505 alumina reheated according to the same procedure as in Example 1.

COMPARATIVE EXAMPLE 2

Preparation of a catalyst of formula K_2WO_4/Al_2O_3 at a concentration of 14 % by weight, equivalent to an alkali metal cation number of
5 92.5 mmol/100 g of catalyst.

The catalyst is prepared according to the method described in Example 1, using 40.23 g of $K_2WO_4 \cdot 2H_2O$ to impregnate 200 g of alumina. The pH of the solution before impregnation is 11.

10 COMPARATIVE EXAMPLE 3

Preparation of a catalyst of formula Na_2WO_4/Al_2O_3 at a concentration of 13.6 % by weight, equivalent to an alkali metal cation number of 92.5 mmol/100 g of catalyst.

15 The catalyst is prepared according to the method described in Example 1, using 36 g of $Na_2WO_4 \cdot 2H_2O$ to impregnate 200 g of alumina. The pH of the solution before impregnation is 9.88.

EXAMPLE 6

20 Catalytic test of the catalysts of Examples 1 to 5 and Comparative Examples 1 to 3.

The catalytic performance of the catalysts described in Examples 1 to 5 and Comparative Examples 1 to 3 were determined under the following conditions.

25 A 90 ml bed, consisting of catalyst in the form of beads having an undiluted diameter of about 3 mm, is contained in a reactor 35 cm in height and 27.3 mm in inside diameter.

The reactor inlet gases consist of a mixture of methanol, hydrogen sulphide, methyl mercaptan, dimethyl sulphide and water in the following molar proportions: 6.5/70.5/11.5/4/7.5%. The gases are first
 5 passed through a bed of 100 ml of corundum beads for preheating to the reaction temperature. The pressure in the reactor is maintained at 10 bar. The reaction temperature is maintained at 320°C.

The HVV or hourly volume velocity, calculated
 10 under standard temperature and pressure conditions, is 6667 h⁻¹, i.e. a contact time of 0.54 s.

The hourly volume velocity, HVV, is defined as the ratio:

Total flow rate of the reactants under standard conditions
 15 volume of catalyst

The degree of conversion of the methanol, X_g, is defined as the ratio:

Number of moles of methanol converted × 100
Number of moles of methanol at the inlet

20 The selectivity towards product i, S_i, is defined as the ratio:

Number of moles of product i formed × 100
Number of moles of methanol converted

The yield of product i, Y_i , is defined as the product $X_g \times S_i$.

The performance of the catalysts of Examples 1 to 5 and Comparative Examples 1 to 3, measured after 100 hours under reactants, is reported in Table 1 below. MSH stands for methyl mercaptan. DMS stands for dimethyl sulfide.

TABLE 1

Example	Catalyst (% by weight)	X_g (%)	SMSh (%)	SDMS (%)	SCO ₂ (%)	YMSH (%)	YDMS (%)
10 C1	alumina alone	100	60	40	0	60	40
1	2 % K ₂ CO ₃	94.0	82.5	17.5	0	77.6	16.5
2	6.4 % K ₂ CO ₃	93.0	93.0	5.0	2.0	86.5	4.7
3	10 % K ₂ CO ₃	78.5	89.5	9.5	1.0	70.3	7.5
4	4.9 % Na ₂ CO ₃	87.0	89.0	10.0	1.0	77.4	8.7
15 5	15.1 % Cs ₂ CO ₃	92.0	94.0	5.0	1.0	86.5	11.0
C2	14 % K ₂ WO ₄	75.0	94.0	4.0	2.0	70.5	3.0
C3	13.6 Na ₂ WO ₄	86.0	87.0	5.0	8.0	74.8	4.3

The methanol conversions and yields of MSH, using the catalysts of Examples 1 to 4 and Comparative Examples 1 and 2, measured at different operating temperatures for a reaction temperature of 370°C (conditions of accelerated ageing) are reported in Table 2 below:

TABLE 2

Example	Catalyst (% by weight)	Duration in hours	Xg (%)	YMSH (%)	-Xg/ Δ t (%) for 100 h
C1	alumina alone	100	100	70.0	0
		150	100	63.0	
		250	100	62.0	
		400	100	57.0	
1	2 % K_2CO_3	100	100	79.0	1
		150	100	77.5	
		250	98.0	77.0	
		400	97.0	75.0	
2	6.4 % K_2CO_3	100	98.0	86.0	0.6
		250	98.0	86.5	
		400	97.5	87.0	
		500	96.0	87.6	
		600	95.0	87.5	
3	10 % K_2CO_3	100	95.0	77.0	1.6
		250	93.0	77.5	
		400	91.0	78.0	
		500	88.0	77.0	
		600	87.0	75.0	
4	4.9 % Na_2CO_3	250	100	88.0	1.4
		400	97.5	86.0	
		500	97.0	87.0	
		600	95.0	86.0	
C2	14 % K_2WO_4	250	90.0	85.0	5
		400	85.0	82.0	
		500	77.0	78.5	
		550	75.0	77.0	

EXAMPLES 6 TO 10 AND COMPARATIVE EXAMPLES 4 TO 8

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An industrial test is performed on an array of 7 reactors preceded by a converter. The converter is charged with Spheralite 505® alumina. The 7 reactors are charged either with the catalyst of Example 2 containing 6.4 % K_2CO_3 or with the catalyst of

Comparative Example 2. 5000 kg/h of a mixture containing, by weight:

84 % hydrogen sulphide

6 % methanol

5 5 % dimethyl sulphide

5 % methyl mercaptan

is introduced into the converter.

300 kg/h of methanol are introduced into each of the 7 reactors. Several tests are performed at different inlet temperatures of the gases into the reactor. The results are shown in Table 3 below:

TABLE 3

Example	Temperature (°C)	Catalyst	Xg	SMSH (%)	SDMS (%)	YMSH (%)
6	230	6.4 % K_2CO_3	63.68	99.40	0.60	63.30
15 C4	230	14 % K_2WO_4	42.97	99.85	0.15	42.90
7	280	6.4 % K_2CO_3	82.77	94.44	5.56	78.17
C5	280	14 % K_2WO_4	63.27	98.56	1.44	62.36
8	310	6.4 % K_2CO_3	91.93	85.54	14.46	78.64
C6	310	14 % K_2WO_4	72.89	96.13	3.87	70.07
20 9	340	6.4 % K_2CO_3	99.15	66.27	33.73	65.70
C7	340	14 % K_2WO_4	82.29	90.48	9.52	74.46
10	370	6.4 % K_2CO_3	100.00	37.77	62.23	37.77
C8	370	14 % K_2WO_4	92.07	78.53	21.47	72.30

It is clear from Tables 1 to 3 that if it is desired to optimize the stability of the catalyst over time and the yield of methyl mercaptan, it is very

advantageous to use a catalyst based on K_2CO_3 at a temperature of between 230 and 330°C and preferably of between 280°C and 310°C.

CLAIMS

1. Process for the preparation of methyl mercaptan by reacting methanol and hydrogen sulphide in the vapour phase in the presence of a catalyst, wherein
5 the catalyst is an alkali metal carbonate deposited on alumina and wherein the reaction is carried out at a temperature below 350°C.

2. Process according to claim 1, wherein the alkali metal carbonate is chosen from sodium
10 carbonate, potassium carbonate and caesium carbonate.

3. Process according to claim 2, wherein the alkali metal carbonate is potassium carbonate.

4. Process according to claim 1, wherein between 2 and 20 % by weight of alkali metal carbonate
15 is deposited on the alumina.

5. Process according to claim 3, wherein between 2 and 10 % by weight of potassium carbonate is deposited on the alumina.

6. Process according to claim 5, wherein
20 about 6.4% by weight of potassium carbonate is deposited on the alumina.

7. Process according to claim 1, wherein the reaction temperature is between 230 and 330°C.

8. Process according to claim 7, wherein
25 the reaction temperature is between 280 and 310°C.

9. Process according to claim 1, wherein the molar ratio of hydrogen sulphide to methanol in the reaction is between 1.5:1 and 2.5:1.



10. Process according to claim 1, wherein the reaction is carried out at a pressure of between 8 and 15 bar (8 to 15×10^5 Pa).

11. Process according to claim 1, wherein
5 the catalyst is distributed in a system comprising at least three reactors.

12. Catalyst for use in the preparation of methyl mercaptan, which is of improved stability and which consists of an alkali metal carbonate deposited
10 on alumina.

13. Catalyst according to claim 12, wherein the alkali metal carbonate is potassium carbonate.

ABSTRACT**PROCESS FOR THE PREPARATION OF METHYL MERCAPTAN**

A process for the preparation of methyl mercaptan by reacting methanol and hydrogen sulphide in the vapour phase in the presence of a catalyst wherein the catalyst is an alkali metal carbonate deposited on alumina and wherein the reaction is carried out at a temperature below 350°C.