

Process for continuously preparing methyl mercaptan
from carbon- and hydrogen-containing compounds

The invention relates to a process for continuously
5 preparing methyl mercaptan by reacting a reactant
mixture which comprises solid, liquid and/or gaseous
carbon- and/or hydrogen-containing compounds with air
or oxygen and/or water and sulphur.

10 Methyl mercaptan is an industrially important
intermediate for the synthesis of methionine and for
the preparation of dimethyl sulphoxide and dimethyl
sulphone. Methyl mercaptan is prepared predominantly
from methanol and hydrogen sulphide by reaction over a
15 catalyst consisting of an aluminium oxide support and
transition metal oxides and basic promoters. The
mercaptan is usually synthesized in the gas phase at
temperatures between 300 and 500°C and at pressures
between 1 and 25 bar. As well as the methyl mercaptan
20 formed and water, the product gas mixture comprises the
unconverted proportions of the methanol and hydrogen
sulphide starting materials, and dimethyl sulphide and
dimethyl ether as by-products, and also small amounts
of polysulphides (dimethyl disulphide). Gases which are
25 inert in the context of the reaction, for example
carbon monoxide, carbon dioxide, nitrogen and hydrogen,
are also present in the product gas.

The methyl mercaptan formed is removed from the product
30 gas mixture, as explained, for example, in US 5866721,
in a plurality of distillation and wash columns at
temperatures between 10 and 140°C.

Methyl mercaptan can alternatively be prepared from
35 carbon oxides, hydrogen, sulphur and/or hydrogen
sulphide. According to US 4665242, for example, methyl
mercaptan is prepared over catalysts based on alkali
metal tungstates. Compared to the methanol-based

process, these processes have lower selectivities for methyl mercaptan and conversions of carbon oxides. US 4410731 relates to a process and to catalysts for the preparation of methyl mercaptan from carbon oxides, hydrogen and hydrogen sulphide or sulphur, based on alkali metal molybdenum sulphides comprising transition metal oxides as promoters, and aluminium oxide as a support. WO 2005/040082 claims a process and catalysts for the preparation of methyl mercaptan from carbon oxides, hydrogen and hydrogen sulphide or sulphur based on alkali metal molybdates comprising transition metal oxides as promoters, in which silicon dioxide preferably serves as a support.

The preparation of methyl mercaptan from carbon disulphide or carbonyl sulphide and hydrogen is a further alternative to the process based on methanol. However, the processes are characterized by comparatively low selectivities for methyl mercaptan, a multitude of by-products which are difficult and costly to remove, and the necessity of handling toxic carbon disulphide or carbonyl sulphide in large amounts.

The direct conversion of mixtures obtained in other processes, which comprise methane or higher hydrocarbons, water, hydrogen and possibly sulphur-containing compounds, to methyl mercaptan has to date not succeeded in industrially relevant yields and selectivities, but rather leads to a multitude of by-products including toxic carbon disulphide as a main component.

What is common to all abovementioned processes is that carbon compounds such as methanol, carbon oxides, or sulphur-containing compounds such as carbonyl sulphide or carbon disulphide, are required as raw materials for the preparation of methyl mercaptan. These constitute a significant cost factor, particularly when the product

selectivities for the formation of methyl mercaptan are comparatively low. Moreover, sometimes complicated purification steps are needed, in which a multitude of secondary components cannot be recycled into the process. This reduces the overall selectivity for methyl mercaptan and thus the economic viability of the process.

The direct conversion of reactants which comprise natural gas (methane), hydrocarbons, for example from heavy oil fractions, residues from crude oil refining, or higher hydrocarbons in general, for example oligomers, polymers or polycyclic aromatics, which are normally, for example, also obtained as waste streams in other chemical processes, with air or oxygen, water and sulphur to give methyl mercaptan is the object of the invention. Compared to the industrially practised methanol-based process, owing to significantly lower raw material costs, it has a significant cost advantage in the variable operating costs. As evident from the above for the person skilled in the art, such a process is not available according to the prior art. As a result of comparatively low product selectivities and a wide spectrum of by-products, and the toxicity of the reaction intermediates, which necessitates extensive safety measures for protection of people and the environment, such a process for preparing methyl mercaptan did not exist.

The economic viability of the overall process depends crucially upon the product selectivity for methyl mercaptan, based on the carbon source used. As a result of the inventive use of carbon- and hydrogen-containing compounds which are obtained as secondary components or as waste streams in other processes or are utilised only as a fuel for energy generation, an additional cost advantage can be achieved. For example, selective oxidations form a series of secondary components which

additionally contain chemically bound oxygen, for example alcohols, aldehydes, carboxylic acids and/or carbon oxides. They are generally incinerated after the removal of the main reaction product or converted in a further chemical reaction such that disposal is possible. Further examples of sources of reactant mixtures are industrial processes for obtaining organic nitrogen or sulphur compounds, in which relatively large amounts of by-products are obtained and generally have to be incinerated or disposed of in another way without further upgrading. In particular, it is possible in the process according to the invention to use offgas streams which comprise H_2S , COS , SO_2 , SO_3 -containing compounds, alkyl sulphides or alkyl polysulphides. These explicitly also include gases which are obtained from waste streams of plants for generating energy or chemical products directly or via separation techniques, or in the course of biological metabolism processes (for example fermentation and degradation processes). These gas mixtures may comprise, as main components, hydrocarbons, carbon oxides, organic sulphur and nitrogen compounds or hydrogen sulphide, as well as other substances, and may be supplied to the process according to the invention.

In a first aspect, there is provided a process for continuously preparing methyl mercaptan by converting a reactant mixture which comprises carbon- and hydrogen-containing compounds, wherein the following process steps are passed through, in which the carbon- and hydrogen-containing compounds are reacted in process step 1 with air or oxygen, optionally with water, to give a gas mixture which comprises carbon dioxide, carbon monoxide and hydrogen, this gas mixture is reacted in process step 2 with liquid or gaseous sulphur in a one-stage or multistage process step at a reaction pressure of at least 5 bar and a temperature of at least 200°C, and the molar $\text{CO}_2/\text{CO}/\text{H}_2/\text{H}_2\text{S}$ ratio is adjusted to a ratio of 1:0.1:1:0 to 1:1:10:10 by feeding in water or hydrogen and optionally hydrogen sulphide, the gas mixture thus obtained having a molar ratio of the compounds $\text{CO}_2/\text{CO}/\text{H}_2/\text{H}_2\text{S}$ of 1:0.1:1;1 to 1:1:10:10 is converted in process step 3 at a reaction pressure of at least 5 bar and a temperature of at least 200°C over a catalyst to a reaction mixture which comprises methyl mercaptan as the main reaction product, this methyl mercaptan is removed in process step 4, and, in process step 5, after removal of the gaseous by-products, the unconverted feedstocks, after optional reaction with water, are recycled into the process, and where the gas mixture leaves the first process step at a pressure of at least 5 bar and is fed directly, without further compression, to the second process step, and the corresponding gas mixtures are subsequently fed at this pressure to the third and fourth process steps.

It is an object of the disclosure to provide an economically viable process for preparing methyl mercaptan from reactant mixtures which comprise
5 carbon- and hydrogen-containing compounds, air or oxygen, and/or water and sulphur.

The disclosure provides a process for continuously preparing methyl mercaptan by
10 converting a reactant mixture which comprises carbon- and hydrogen-containing compounds, wherein the following process steps are passed through, in which the carbon- and hydrogen-containing compounds are reacted in process step
15 1 with air or oxygen, optionally with water, to give a gas

mixture which comprises carbon dioxide, carbon monoxide and hydrogen as main components.

5 The carbon-containing compounds may be provided in the solid, liquid or gaseous state, but are preferably in gaseous form at the time of the reaction.

In addition, the reactant gas may comprise organic sulphur compounds or H_2S .

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CO , CO_2 and hydrogen are present in the gas mixture leaving process step 1 generally in an amount of 1 to 90% by volume.

15 Preference is given to concentrations of 5 to 25% by volume for CO , 5 to 50% by volume for CO_2 and of 10 to 90% by volume for H_2 , the total amount remaining being preferably < 100% by volume, especially ~ 90% by volume.

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Subsequently, this gas mixture is reacted directly, without further compression and workup of the gases, at a reaction pressure of at least 5 bar and a temperature of at least 200°C, with liquid or gaseous sulphur in a one-stage or multistage process step 2.

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The molar $CO_2/CO/H_2/H_2S$ ratio is adjusted to a ratio of 1:0.1:1:0 to 1:1:10:10 by feeding in water or hydrogen and optionally hydrogen sulphide.

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In process step 3, this gas mixture is converted at a reaction pressure of at least 5 bar and a temperature of at least 200°C over a catalyst to a reaction mixture which comprises methyl mercaptan as the main product.

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Subsequently, the methyl mercaptan is removed by processes known per se in process step 4.

In process step 5, after removal of the gaseous by-products, the unconverted feedstocks, after optional reaction with water, are recycled into the process.

5 The overall selectivity for methyl mercaptan can be increased by recycling carbon-, hydrogen- and sulphur-containing compounds into the first, second or third process step. Preference is given to recycling carbon oxides, hydrogen, carbonyl sulphide and hydrogen
10 sulphide into the second or third process step, while by-products, for example water, hydrocarbons and other sulphur-containing compounds, for example (poly)sulphides and carbon disulphide, are recycled into the first process step. It is a particular
15 advantage of the invention that (poly)sulphides and toxic carbon disulphide occur with selectivities of less than 1% and, as a result of the recycling into the process, do not have to be separated and disposed of in a technically complicated and costly manner.

20 As well as the methyl mercaptan formed and water, the product gas mixture of the third process step comprises the unconverted carbon dioxide, carbon monoxide, hydrogen and hydrogen sulphide starting materials and,
25 as by-products, carbonyl sulphide, methane, dimethyl sulphide and also small amounts of polysulphides (dimethyl disulphide) and carbon disulphide. Gases which are inert in the context of the reaction, for example nitrogen and hydrocarbons, are also present in
30 the product gas.

The methyl mercaptan formed is removed from the product gas mixture, for example as explained in DE-A-1768826, in several distillation and wash columns at
35 temperatures between 10 and 140°C. Carbon dioxide, carbon monoxide, hydrogen, hydrogen sulphide and, as by-products, carbonyl sulphide, methane, dimethyl sulphide and also small amounts of polysulphides

(dimethyl disulphide) and carbon disulphide, are recycled into the first, second or third process step. Advantageously, the stream is reacted in an optional fifth process step, preferably catalytically, with
5 water in such a way that the cycle gas recycled into the process only comprises the main components CO_2 , CO , H_2 and H_2S .

The economic viability of the overall process is
10 increased by the fact that, advantageously, no complicated and costly removal of potential catalyst poisons, for example sulphur-containing compounds and elemental sulphur, is needed before the metered addition of the feedstocks to the first and second
15 process step. Equally, a removal of such compounds after the reaction in the first process stage is unnecessary. These substances can be fed directly to the second process step together with the reaction gases, without further workup and compression of the
20 gases, which constitutes a significant cost advantage with regard to the capital and operating costs of the process. There is thus no costly desulphurization of the reactant and product mixture of the first process step. Advantageously, sulphur or sulphur-containing
25 slags which may be obtained as by-products of process step 1 can be fed directly in solid, liquid or gaseous form as a reactant to process step 2. This explicitly also includes gases which are obtained from offgas streams of plants for generating energy or chemical
30 products directly or via separation techniques, or form in the course of biological degradation and metabolism processes and can be fed directly to the second process step. These gas mixtures may comprise, as main components, hydrocarbons, carbon oxides, sulphur and
35 nitrogen compounds in a total concentration of 5 to 90% by volume in addition to other substances, and may be fed to process steps 1, 2 or 3.

The gas mixture can be converted in the second process stage, optionally with use of a catalyst, by reaction with liquid or gaseous sulphur in a one-stage or multistage process step. In the second process step, full conversion of hydrogen is not attempted. The reaction is performed such that, after the reaction, the $\text{CO}_2/\text{CO}/\text{H}_2/\text{H}_2\text{S}$ ratio is 1:0.1:1:1 to 1:1:10:10. Advantageously, the reaction gas from the first process step leaves it at a pressure of at least 5 bar and can be fed directly without further compression to the second process step. This constitutes a significant cost advantage, since it is possible to dispense with a compressor stage with high capital and operating costs. The reaction gas mixture from the second process step is subsequently fed to the third process step without further compression and workup of reaction products. Optionally, apparatus for removing elemental sulphur or sulphur-containing compounds can be connected upstream of this process step. The conversion to methyl mercaptan is effected in a third process step over catalysts. Advantageous catalysts in the second and third process step have been found to be metal oxide catalysts. Preference is given to using catalysts based on alkali metal molybdates or alkali metal tungstates, which may be applied to supports (US 5852219). Especially suitable are supported catalysts which comprise oxidic Mo compounds and K compounds, where Mo and K may be present in one compound, for example K_2MoO_4 , and at least one active oxidic compound of the general formula A_xO_y . In this formula, A is an element of the manganese group, especially Mn or Re, and x and y are integers of 1 to 7. The catalyst comprises the compounds preferably in a weight ratio of $\text{A}_x\text{O}_y/\text{K}_2\text{MoO}_4/\text{support} = (0.001-0.5)/(0.01-0.8)/1$ or $\text{A}_x\text{O}_y/\text{MoO}_3/\text{K}_2\text{O}/\text{support} = (0.0001-0.5)/(0.01-0.8)/(0.005-0.5)/1$, the weight ratios preferably being in the range of $\text{A}_x\text{O}_y/\text{K}_2\text{MoO}_4/\text{support} = (0.001-0.3)/(0.05-0.5)/1$ or $\text{A}_x\text{O}_4/\text{MoO}_3/\text{K}_2\text{O}/\text{support} = (0.001-0.3)/(0.05-0.3)/(0.03-0.3)/1$.

These catalysts preferably comprise one or more promoters selected from the group or the oxidic compounds with the general formula M_xO_y in which M is a transition element or a metal from the group of the rare earths, and x and y are each an integer of 1 to 7, according to the degree of oxidation of the elements M used.

M is preferably Fe, Co, Ni, La or Ce. In a particular embodiment, M may also be Sn. The ratios of the proportions by weight are in the ranges of:

$$K_2MoO_4/M_xO_y/support = (0.01-0.80)/(0.01-0.1)/1,$$

$$MoO_3/K_2O/M_xO_y/support = (0.10-0.50)/(0.10-0.30)/$$

$$(0.01-0.1)/1.$$

When these catalysts are exposed to an H_2S -containing atmosphere before use, the oxidic metal compounds, which do not mean the support material, are converted to sulphidic compounds or mixtures of oxidic and sulphidic compounds which can likewise be used in accordance with the invention.

The support materials used are preferably silicon dioxides, titanium dioxides, zeolites or activated carbons. When the support used is aluminium oxide, the catalyst comprises rhenium oxides and/or rhenium sulphide(s).

Titanium dioxide is preferably used with a content of 60 mol% of anatase.

The preparation is effected in a multistage impregnation process, with which soluble compounds of the desired promoters or active oxidic compounds are applied to the support. The impregnated support is subsequently dried and optionally calcined.

The second and third process step are preferably combined in one reaction apparatus. This can be done using different or identical catalysts. Advantageously, bubble columns, reactive distillations, fixed bed
5 reactors, staged reactors or tube bundle reactors are used for the catalysed conversion to methyl mercaptan.

The reaction in the second process step is effected at a temperature of 200 to 600°C, especially 250 to 500°C,
10 and a pressure of 1.5 to 50 bar. An operating pressure of 2.5 to 40 bar is preferably established. The conversion to methyl mercaptan is effected in the third process step over catalysts based on alkali metal molybdates or alkali metal tungstates. At a temperature
15 of 200 to 600°C, preferably 250 to 400°C, and a pressure of 1.5 to 50 bar, preferably 8 to 40 bar. Catalysts which are used advantageously in the second and third process step are described in applications WO 2005/040082, WO 2005/021491, WO 2006/015668 and
20 WO 2006/063669.

In a further embodiment of the invention, the second and third process step are combined in one apparatus.

25 The product gas mixture can be separated by various known processes. A particularly advantageous separation is described in the patent EP-B-0850923 (US 5866721).

Unconverted carbon oxides, hydrogen and hydrogen
30 sulphide, and also gaseous by-products, for example carbonyl sulphide and methane, and also higher hydrocarbons, are recycled into the process. This can be done into the reactant stream of the first, second or third process stage. Advantageously, before
35 recycling into the second or third process stage, the CO₂/CO/H₂/H₂S ratio is adjusted to from 1:0.1:1:1 to 1:1:10:10 by reaction with water. This can be done with or without catalysis in a fixed bed reactor, a reaction

tube, a wash column or a reactive distillation at a temperature of at least 120°C. Advantageously, secondary components, for example carbonyl sulphide and carbon disulphide, are hydrolysed in this process step to carbon dioxide and hydrogen sulphide, which re-enter into the second or third process step as reactants. Reaction components, for example sulphides, polysulphides and hydrocarbons, which are obtained during the removal of methyl mercaptan in the fourth process step, can be recycled without further workup into the first or second process step, which increases the overall selectivity of the process for methyl mercaptan, based on carbon, to more than 95%.

Figure 1 serves to further explain the process using the sequence of reaction steps used with preference. What is important for the economic viability of the process is the possibility of using a multitude of solid, liquid and/or gaseous carbon- and hydrogen-containing starting materials, which are metered into the first process step, and the fact that this stream need not be purified and desulphurized in a complicated manner. Moreover, all by-products which are removed in the fourth process step are recycled into the first, second or third process step. Advantageously, all process steps proceed in the same pressure range, such that it is possible to dispense with a costly compression of the gases between the individual process steps. The reactions are effected at the starting pressure of the gases which leave the first process step or are metered into the second or third process step from other sources under process pressure. Advantageously, this pressure is adjusted to from 8 to 40 bar. Gases which are inert in the context of the process are discharged from the process continuously or discontinuously via a purge gas stream.

Example 1:

Steam reformation of a hydrocarbon feed gas stream and subsequent reaction with sulphur afforded a gas mixture which comprises the main components $\text{CO}_2/\text{CO}/\text{H}_2/\text{H}_2\text{S}$ in a ratio of $\sim 1/0.1/4/4$. At a reaction temperature of 250-350°C and a pressure of 30 bar, the reactants were converted in the third process step over various catalysts. The catalytic activity was initially determined for a single pass through the reactor.

Table 1

Catalyst	Conversion (CO_2) / %	Selectivity (MC) / %	Selectivity (CO) / %	Selectivity (CH_4) / %
Catalyst A $\text{Re}_2\text{O}_7/\text{K}_2\text{MoO}_4/\text{TiO}_2$	55.8	82.2	11.8	4.5
Catalyst B $\text{SnO}_2/\text{Re}_2\text{O}_7/\text{K}_2\text{MoO}_4/\text{TiO}_2$	53.5	82.6	9.9	4.8
Catalyst C $\text{Mn}_x\text{O}_y/\text{K}_2\text{MoO}_4/\text{TiO}_2$	50.1	81.5	12.6	3.5

CO_2 = carbon dioxide

MC = methyl mercaptan

Example 2:

Methyl mercaptan was removed from the product gas stream (process step 4) of Example 1. The return gas comprising the main components CO_2 , H_2 , CO and H_2S was, after reaction with water in reaction step 5, recycled into process step 3 and converted under analogous reaction conditions to those in Example 1. Over catalysts A-C, methyl mercaptan selectivities of 90-94% were achieved.

Claims

1. Process for continuously preparing methyl mercaptan by converting a reactant mixture which comprises carbon- and hydrogen-containing compounds, wherein the following process steps are passed through, in which the carbon- and hydrogen-containing compounds are reacted in process step 1 with air or oxygen, optionally with water, to give a gas mixture which comprises carbon dioxide, carbon monoxide and hydrogen, this gas mixture is reacted in process step 2 with liquid or gaseous sulphur in a one-stage or multistage process step at a reaction pressure of at least 5 bar and a temperature of at least 200°C, and the molar $\text{CO}_2/\text{CO}/\text{H}_2/\text{H}_2\text{S}$ ratio is adjusted to a ratio of 1:0.1:1:0 to 1:1:10:10 by feeding in water or hydrogen and optionally hydrogen sulphide, the gas mixture thus obtained having a molar ratio of the compounds $\text{CO}_2/\text{CO}/\text{H}_2/\text{H}_2\text{S}$ of 1:0.1:1:1 to 1:1:10:10 is converted in process step 3 at a reaction pressure of at least 5 bar and a temperature of at least 200°C over a catalyst to a reaction mixture which comprises methyl mercaptan as the main reaction product, this methyl mercaptan is removed in process step 4, and, in process step 5, after removal of the gaseous by-products, the unconverted feedstocks, after optional reaction with water, are recycled into the process, and where the gas mixture leaves the first process step at a pressure of at least 5 bar and is fed directly, without further compression, to the second process step, and the corresponding gas mixtures are subsequently fed at this pressure to the third and fourth process steps.
2. Process according to Claim 1, wherein the reactant mixture comprises nitrogen-containing compounds.
3. Process according to Claim 1 or 2, wherein the reactant mixture comprises sulphur-containing compounds.

4. Process according to Claims 1 to 3, in which the reactant mixture comprises compounds which are carbon-, hydrogen- and oxygen-containing.
- 5 5. Process according to Claims 1 to 4, in which the carbon- and hydrogen-containing and optionally oxygen-containing compounds are converted by partial oxidation with air or oxygen or by steam reformation to gas mixtures which comprise CO₂,
10 CO, H₂ and optionally H₂S.
6. Process according to Claims 1 to 5, in which the compounds present in the reactant mixture stem from offgas streams of processes for generating
15 energy or chemical products.
7. Process according to Claim 6, in which streams from the workup of processes for oxidation of hydrocarbons and for synthesis of nitrogen- and
20 sulphur-containing compounds are supplied to the process as raw materials.
8. Process according to Claims 1 to 6, wherein gas mixtures generated in biological metabolism
25 processes are introduced into process steps 2 or 3.
9. Process according to Claim 6, 7 or 8, in which the gas mixtures comprise at least one compound
30 selected from the group of methane, higher hydrocarbons having a C₂-C₆ radical, CO₂ and CO.
10. Process according to Claims 1 to 3, in which the conversion to a gas mixture which comprises CO₂,
35 CO, H₂ and H₂S in process step 2 is effected in the presence of liquid or gaseous sulphur in a one-stage or multistage uncatalysed homogeneous reaction or using a catalyst.

11. Process according to Claims 1 to 10, characterized in that the $\text{CO}_2/\text{CO}/\text{H}_2/\text{H}_2\text{S}$ ratio at the end of process step 2 ranges from 1:1:1:1 to 1:0.1:4:4.
12. Process according to Claims 1 to 11, in which the methyl mercaptan is removed from the reaction gas and unconverted gaseous feedstocks are recycled into process steps 1, 2 or 3.
13. Process according to Claims 1 to 12, in which carbon-, hydrogen- and sulphur-containing reaction by-products are recycled into process steps 1, 2 or 3.
14. Process according to Claims 1 to 12, in which the total amount of hydrogen sulphide in process step 3 is established by varying the carbon-hydrogen ratio of the compounds present in the reactant mixture or the H_2 content in the reaction gas which is fed to reaction stage 2, and by varying one or more process parameters selected from the group of: residence time, reaction temperature and reaction pressure.
15. Process according to Claims 1 to 4, in which, in process steps 2 and 3, reactive distillations, bubble column reactors, fixed bed reactors, staged reactors or tube bundle reactors are used for the catalysed conversion to methyl mercaptan.
16. Process according to Claims 1 to 5, in which process steps 2 and 3 are combined in one reaction apparatus.
17. Process according to Claim 1, in which, after the first and the second process step, no sulphur-containing compounds are removed.

18. Process according to Claim 1, in which the overall selectivity for carbon disulphide and (poly)sulphides is less than 1%.
- 5 19. Process according to Claims 1 to 18, in which catalysts which comprise alkali metal tungstates, alkali metal molybdates or halide-containing alkali metal tungstates or alkali metal molybdates which comprise transition metal oxides or
10 sulphides as promoters are used.
20. Process according to Claims 1 to 18, in which the gas mixture is converted in process step 3 over molybdate- or tungstate-containing catalysts which
15 comprise transition metal oxides or sulphides and alkali metal oxides or sulphides as promoters.
21. Process according to Claim 19, in which at least one of the promoters selected from the group of
20 alkali metal tungstates, alkali metal molybdates or halide-containing alkali metal tungstates or alkali metal molybdates which comprise cobalt oxides or sulphides, manganese oxides or sulphides and rhenium oxides or sulphides is used as a
25 catalyst.
22. Process according to Claims 1 to 18, in which supported catalysts which comprise oxidic Mo and K compounds are used, where Mo and K may be present
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in one compound, and which comprise at least one active oxidic compound of the general formula A_xO_y , A is an element of the manganese group, especially Mn or Re, and x and y are integers of 1 to 7.

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23. Process according to Claims 1 to 18 and 22, in which the catalysts comprise the compounds preferably in a weight ratio of
- 10 $A_xO_y/K_2MoO_4/support = (0.001-0.5)/(0.01-0.8)/1$ or $A_xO_4/MoO_3/K_2O/support = (0.001-0.5)/(0.01-0.8)/(0.005-0.5)/1$.
- 15 24. Process according to Claims 1 to 18 and 22, 23, wherein the weight ratios are preferably within the range of
- $A_xO_y/K_2MoO_4/support = (0.001-0.3)/(0.05-0.5)/1$ or $A_xO_4/MoO_3/K_2O/support = (0.001-0.3)/(0.05-0.3)/(0.03-0.3)/1$.
- 20 25. Process according to Claims 1 to 18 and 22 to 24, wherein the catalysts comprise one or more promoters selected from the group of the oxidic compounds with the general formula M_xO_y in which M is a transition element or a metal from the group
- 25 of the rare earths, and x and y are each an integer of 1 to 7.
26. Process according to Claims 1 to 18 and 22 to 25, wherein the ratios of the proportions by weight
- 30 are within the ranges of:
- $K_2MoO_4/M_xO_y/support = (0.01-0.80)/(0.01-0.1)/1$,
 $MoO_3/K_2O/M_xO_y/support = (0.10-0.50)/(0.10-0.30)/(0.01-0.1)/1$, where x and y are each an integer of
- 35 1 to 7.
27. Process according to Claim 26, wherein the ratios are within the ranges of $K_2MoO_4/M_xO_y/support = (0.10-0.60)/(0.01-0.06)/1$,

$\text{MoO}_3/\text{K}_2\text{O}/\text{M}_x\text{O}_y/\text{support} = (0.10-0.30)/(0.10-0.25)/$
 $(0.01-0.06)/1.$

28. Process according to Claims 1 to 27, wherein these
5 catalysts are exposed to an H_2S -containing
atmosphere before use.