

101081994 A and US 2011/0015060 A1 only show a poor catalytic activity in the oxidation of methylmercaptan or dimethyldisulfide with oxygen. Accordingly, these catalysts are not suitable for use in the industrial preparation of alkanesulfonic acids.

- 5 The published patent application CN 102600903 A discloses desulfurization catalysts on the basis of vanadium liquid phase catalysts comprising a vanadium compound and a carrier which is an organic amine. A suitable vanadium compound is the combination of sodium vanadate and ammonium vanadate.
- 10 It is therefore an object of the present invention to provide a more efficient catalyst for the oxidation of sulfur containing hydrocarbon compounds, preferably of methylmercaptan and/or dimethyldisulfide, with oxygen to alkanesulfonic acids.

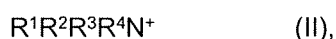
- It was found that the replacement of tungsten in the aforementioned catalysts with vanadium significantly changes the activity of the thus obtained catalyst with respect to the oxidation of sulfur containing hydrocarbon compounds.
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One object of the present invention is therefore a catalyst according to the general formula (I)

- 20 $Q_a[M_b(VO_4)_c]^{a-}$ (I),

wherein

Q is a quaternary ammonium cation of the general formula (II)



- 25 wherein each of R^1 , R^2 , R^3 and R^4 is independently of each other a saturated C_1 to C_{20} alkyl radical or an aromatic C_5 or C_6 radical with the proviso that at least one of R^1 , R^2 , R^3 and R^4 is a saturated C_4 to C_{20} alkyl group,

M is at least one metal selected from the group consisting of Mg, Co, Cu, Fe, Ba and Zr,

V denotes vanadium,

- 30 O denotes oxygen,

a is the integer 1 or 3,

b is the integer 1 or 2,

and

integers 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, and 18. Preferably, n is the integer 4, 8, 12, 16 or 18, especially n is the integer 16.

Therefore, in a preferred embodiment of the present invention Q is selected from the group of
5 quaternary ammonium cations consisting of $(C_4H_9)_4N^+$, $(C_4H_9)_3(CH_3)N^+$, $(C_4H_9)_2(CH_3)_2N^+$,
 $(C_4H_9)(CH_3)_3N^+$, $(C_8H_{17})_4N^+$, $(C_8H_{17})_3(CH_3)N^+$, $(C_8H_{17})_2(CH_3)_2N^+$, $(C_8H_{17})(CH_3)_3N^+$, $(C_{12}H_{25})_4N^+$,
 $(C_{12}H_{25})_3(CH_3)N^+$, $(C_{12}H_{25})_2(CH_3)_2N^+$, $(C_{12}H_{25})(CH_3)_3N^+$, $(C_{16}H_{33})_4N^+$, $(C_{16}H_{33})_3(CH_3)N^+$,
 $(C_{16}H_{33})_2(CH_3)_2N^+$, $(C_{16}H_{33})(CH_3)_3N^+$, $(C_{18}H_{37})_4N^+$, $(C_{18}H_{27})_3(CH_3)N^+$, $(C_{18}H_{37})_2(CH_3)_2N^+$,
 $(C_{18}H_{37})(CH_3)_3N^+$ and $((C_{18}H_{37})_{75\%}(C_{16}H_{33})_{25\%})_2(CH_3)_2N^+$.

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It was also found that good yields for the formation of alkanesulfonic acids are in particular achieved, when the quaternary ammonium cation in the catalyst contains at least one saturated C_{16} alkyl radical.

15 Therefore, in a further preferred embodiment of the present invention Q is $(C_{16}H_{33})_4N^+$, $(C_{16}H_{33})_3(CH_3)N^+$, $(C_{16}H_{33})_2(CH_3)_2N^+$ or $(C_{16}H_{33})(CH_3)_3N^+$.

By far the best results for the production of alkanesulfonic acids were obtained, when the quaternary ammonium cation in the catalyst contains at least one saturated C_{16} alkyl radical and a methyl radical.

20 The most efficient catalyst contains one saturated C_{16} alkyl radical and three methyl groups in its quaternary ammonium cation.

Therefore, the quaternary ammonium cation Q in the catalyst of the present invention is preferably $(C_{16}H_{33})(CH_3)_3N^+$.

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It was found that the presence of a metal M, which is selected from Mg, Co, Cu, Fe, Ba and Zr, in the catalyst of the present invention significantly contributes to their catalytic activity in the oxidation of sulfur containing hydrocarbon compounds with oxygen, for example in the oxidation of dimethyldisulfide as an exemplary representative of the dialkyldisulfides.

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In the oxidation of dimethyldisulfide, as a representative dialkyldisulfide, catalyst in which the metal M is Mg showed the highest conversion rate for the sulfur containing starting compound and the highest yield for the desired alkanesulfonic acid.

10 Therefore, in an embodiment of the present invention the metal M is Mg.

The catalyst according to the present invention comprises a vanadate ion VO_4^{3-} and a quaternary ammonium cation Q of the formula $\text{R}^1\text{R}^2\text{R}^3\text{R}^4\text{N}^+$, with the above identified definitions. Depending on the valence of the metal ions comprised therein, the catalyst of the present invention comprises preferably one or two vanadate ions and one or three quaternary ammonium cations Q. The latter is for example the case when M is Al. However, with M being a metal selected from the group consisting of Mg, Co, Cu, Fe, Ba and Zr, the catalyst of the present invention comprises one vanadium ion and one quaternary ammonium cation Q.

20 Therefore, in another preferred embodiment of the present invention a is 1, b is 1 and c is 1.

Thus, the catalyst of the present invention preferably corresponds to the general formula (I)
 $\text{Q}[\text{MVO}_4]^- \quad (\text{I})$

25 wherein

Q is selected from the group of quaternary ammonium cations consisting of $(\text{C}_4\text{H}_9)_4\text{N}^+$, $(\text{C}_4\text{H}_9)_3(\text{CH}_3)\text{N}^+$, $(\text{C}_4\text{H}_9)_2(\text{CH}_3)_2\text{N}^+$, $(\text{C}_4\text{H}_9)(\text{CH}_3)_3\text{N}^+$, $(\text{C}_8\text{H}_{17})_4\text{N}^+$, $(\text{C}_8\text{H}_{17})_3(\text{CH}_3)\text{N}^+$, $(\text{C}_8\text{H}_{17})_2(\text{CH}_3)_2\text{N}^+$, $(\text{C}_8\text{H}_{17})(\text{CH}_3)_3\text{N}^+$, $(\text{C}_{12}\text{H}_{25})_4\text{N}^+$, $(\text{C}_{12}\text{H}_{25})_3(\text{CH}_3)\text{N}^+$, $(\text{C}_{12}\text{H}_{25})_2(\text{CH}_3)_2\text{N}^+$, $(\text{C}_{12}\text{H}_{25})(\text{CH}_3)_3\text{N}^+$, $(\text{C}_{16}\text{H}_{33})_4\text{N}^+$,

formula $R-S-S-R$ or $R-S_2-R$, and dialkylpolysulfides have the general formula $R-S_n-R$, with n being an integer from 3 to 9. In context of the present of the present invention the two alkyl groups in a dialkyldisulfide and in dialkylpolysulfide are identical, in other words the dialkyldisulfide and the dialkylpolysulfide are symmetrical compounds. The alkyl radical R in each of the alkylmercaptans, dialkyldisulfides and dialkylpolysulfides is a saturated C_1 to C_{20} alkyl group, preferably a C_1 to C_{10} alkyl group, preferably a C_1 to C_4 alkyl group, such as a methyl, ethyl, *n*-propyl, iso-propyl, *n*-butyl, iso-butyl or tert-butyl group.

The catalyst of the present invention is obtainable by combining solutions of suitable precursor compounds or salts containing the specific elements or specific chemical entities of the desired catalyst. Typically, solutions of salts of the metal M in nitric acid are prepared at room temperature and stirred for a time which is sufficient for homogenizing the solution, e.g. 10 minutes. Suitable salts of the metal M are for example nitrate salts. Following, a salt of the quaternary ammonium cation Q , preferably a halogen salt, is added to the mixture and stirred for a time which is sufficient for homogenizing the solution, e.g. 30 minutes. Finally, a solution of an orthovanadate salt, preferably an alkali salt or alkaline earth salt of an orthovanadate, is added to the mixture, and the thus obtained mixture is stirred at room temperature for a time which is sufficient for homogenizing the solution, e.g. 24 hours. Alternatively, the sequence of adding the salt of the quaternary ammonium cation Q and the orthovanadate solution can be changed. Typically, the obtained mixture is concentrated under reduced pressure to give the catalytically active mass, which is finally dried.

Therefore, a further object of the present invention is a method for the production of the catalyst according to the present invention, which comprises the steps of

- a) providing a solution of a salt of the metal M in nitric acid,
- b) adding a salt of the quaternary ammonium cation Q to the solution obtained in step a),
- c) adding a solution of a salt of an orthovanadate to the solution obtained in step b),
- d) stirring the solution obtained in step c),
- e) concentrating the solution of step d) under reduced pressure to give a catalytically active mass, and
- f) drying the catalytically active mass obtained in step e),

wherein the sequence of the steps b) and c) can be changed.

As already mentioned above, the sequence of adding the salt of the quaternary ammonium cation Q (step b) and adding the solution of a salt of an orthovanadate (step c) can be changed. In other words, it is also possible to perform the step c) before the step b).

- 5 In general, the method of the present invention is not subjected to any limitations regarding the choice of the salt of the metal M. Thus, M is a metal selected from the group consisting of alkali metals, alkaline earth metals, group III metals and transition metals.

- 10 However, in accordance with the catalyst according to the present invention, the metal nitrate in step a) is preferably a nitrate of a metal, which is selected from the group consisting of Mg, Co, Cu, Fe, Ba and Zr.

- 15 According to the present invention the catalyst of the present invention and the catalyst obtainable and/or obtained by the method of the present invention are suitable for the catalysis of oxidation reactions, preferably, the catalysis of sulfur containing hydrocarbon compounds. Particularly, the catalyst of the present invention and the catalyst obtainable and/or obtained by the method of the present invention are suitable for the oxidation of alkylmercaptans to dialkyldisulfides and/or alkanesulfonic acids or the oxidation of dialkyldisulfides to alkanesulfonic acids or the oxidation of dialkylpolysulfides to alkanesulfonic acids with oxygen or hydrogen peroxide, preferably oxygen, as
20 oxidizing agent in the presence or absence of nitric acid. Especially, the catalysts of the present invention are suitable for the oxidation of methylmercaptan to dimethyldisulfide and/or methanesulfonic acid, or the oxidation of dimethyldisulfide to methanesulfonic acid with oxygen or hydrogen peroxide, preferably oxygen, as oxidizing agent in the presence or absence of nitric acid.

- 25 Therefore, another object of the present invention is the use of a catalyst of the present invention or of a catalyst obtainable and/or obtained by a method of the present invention in the oxidation of sulfur containing hydrocarbon compounds.

Examples:

I. Preparation of the catalysts

- 5 Example 1: Preparation of $C_{16}H_{33}(CH_3)_3N^+[MgVO_4]^-$ (Mg-V catalyst)

Magnesium nitrate hexahydrate (0.53 g) and a solution of nitric acid (30 ml, 0.1 mol/l) were placed in a 100 l flask. The thus obtained mixture was stirred for 30 minutes and afterwards, hexadecyltrimethylammonium chloride (0.33 g) was added to this mixture and the resulting
10 suspension was stirred for another 60 minutes. To this suspension, a solution of sodium orthovanadate dodecahydrate (4 g) in nitric acid (20 ml, 0.1 g/l) was added and the resulting mixture was stirred at room temperature for 24 hours. Subsequently, the mixture was concentrated under reduced pressure using a rotary evaporator and dried at 100°C for 4 hours.

- 15 Example 2: Preparation of $C_{16}H_{33}(CH_3)_3N^+[CoVO_4]^-$ (Co-V catalyst)

Cobalt nitrate hexahydrate (2.33 g) was dissolved in nitric acid (120 ml, 0.1 mol/l) at room temperature. The resulting solution was placed in a 500 ml flask and stirred for 10 minutes. Subsequently, a solution of sodium orthovanadate dodecahydrate (16 g) in water (80 ml) was added
20 and the thus obtained suspension was stirred for 30 minutes. To this suspension, hexadecyltrimethylammonium chloride (1.28 g) was added and the resulting mixture was stirred at room temperature for 24 hours. Afterwards, the mixture was concentrated under reduced pressure using a rotary evaporator and dried at 100°C for 4 hours.

- 25 Example 3: Preparation of $C_{16}H_{33}(CH_3)_3N^+[CuVO_4]^-$ (Cu-V catalyst)

The Cu-V catalyst was prepared using the procedure of example 2, except that cobalt nitrate hexahydrate was replaced with cupric nitrate hydrate (1.93 g).

- 30 Example 4: Preparation of $(C_{16}H_{33}(CH_3)_3N^+)_3[Fe(VO_4)_2]^{3-}$ (Fe-V catalyst)

Iron(III) nitrate nonahydrate (4 g) was placed in a 100 ml flask, dissolved in nitric acid (30 ml, 0.1 mol/l) at room temperature and the resulting solution stirred for 30 minutes. A

Example 16: Oxidation using the Zr-V catalyst under oxygen atmosphere (40 bar)

A reaction mixture of dimethyldisulfide (15.14 g), acetonitrile (150 g) and the Zr-V catalyst of example 6 (0.15 g) was placed in a 500 ml autoclave and stirred at 90°C under an oxygen atmosphere (40 bar) for 24 hours. The conversion of dimethyldisulfide was 11% (based on results obtained through gas chromatography) and the yield for the formation of methanesulfonic acid was 6.5%.

Example	Catalyst	T [°C]	p(O ₂) [bar]	C _{DMDS} [%]	Yield [%]	
					MSA	H ₂ SO ₄
comp. example 9	—	90	10	4.4	0.88	0
comp. example 10	—	90	40	0.4	0.87	0
example 10	C ₁₆ H ₃₃ (CH ₃) ₃ N ⁺ [MgVO ₄] ⁻	90	10	73	53.7	0.03
example 11	C ₁₆ H ₃₃ (CH ₃) ₃ N ⁺ [MgVO ₄] ⁻	90	40	73	56	0.2
example 12	C ₁₆ H ₃₃ (CH ₃) ₃ N ⁺ [CoVO ₄] ⁻	90	40	16	8.7	0
example 13	C ₁₆ H ₃₃ (CH ₃) ₃ N ⁺ [CuVO ₄] ⁻	90	40	37	22.4	0.72
example 14	(C ₁₆ H ₃₃ (CH ₃) ₃ N ⁺) ₃ [Fe(VO ₄) ₂] ³⁻	90	40	20	11.3	0.16
example 15	C ₁₆ H ₃₃ (CH ₃) ₃ N ⁺ [BaVO ₄] ⁻	90	40	32	10.2	0
example 16	C ₁₆ H ₃₃ (CH ₃) ₃ N ⁺ [ZrVO ₄] ⁻	90	40	11	6.5	0

Table 2: Results of the comparative examples 9 and 10 and of the examples 10 to 16

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II. Catalyst activity in the oxidation of methylmercaptan with oxygen to dimethyldisulfide and methanesulfonic

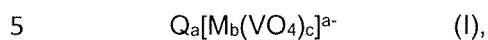
Example 17: Oxidation using the Mg-V catalyst

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A solution of methylmercaptan in acetonitrile (9.1%, 150 g) was placed in a 500 ml autoclave and the Mg-V catalyst C₁₆H₃₃(CH₃)₃N⁺[MgVO₄]⁻ (0.15 g) was added at room temperature. The reaction mixture was stirred at 90°C under an oxygen atmosphere (40 bar) for 24 hours. Following, the reaction mixture was cooled to room temperature and analyzed. The

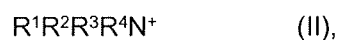
Patent claims

1. Catalyst according to the general formula (I)



wherein

Q is a quaternary ammonium cation of the general formula (II)



10 wherein each of R^1 , R^2 , R^3 and R^4 is independently of each other a saturated C_1 to C_{20} alkyl radical or an aromatic C_5 or C_6 radical with the proviso that at least one of R^1 , R^2 , R^3 and R^4 is a saturated C_4 to C_{20} alkyl group,

M is at least one metal selected from the group consisting of Mg, Co, Cu, Fe, Ba and Zr,

V denotes vanadium,

15 O denotes oxygen,

a is the integer 1 or 3,

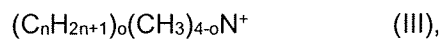
b is the integer 1 or 2,

and

c is the integer 1 or 2.

20

2. Catalyst according to claim 1, wherein Q is a quaternary ammonium cation according to the general formula (III)



wherein

25 n is an integer from 4 to 18, and

o is an integer from 1 to 4.

3. Catalyst according to claim 2, wherein Q is selected from the group of quaternary ammonium cations consisting of $(C_4H_9)_4N^+$, $(C_4H_9)_3(CH_3)N^+$, $(C_4H_9)_2(CH_3)_2N^+$, $(C_4H_9)(CH_3)_3N^+$, $(C_8H_{17})_4N^+$, $(C_8H_{17})_3(CH_3)N^+$, $(C_8H_{17})_2(CH_3)_2N^+$, $(C_8H_{17})(CH_3)_3N^+$, $(C_{12}H_{25})_4N^+$, $(C_{12}H_{25})_3(CH_3)N^+$, $(C_{12}H_{25})_2(CH_3)_2N^+$, $(C_{12}H_{25})(CH_3)_3N^+$, $(C_{16}H_{33})_4N^+$, $(C_{16}H_{33})_3(CH_3)N^+$, $(C_{16}H_{33})_2(CH_3)_2N^+$, $(C_{16}H_{33})(CH_3)_3N^+$, $(C_{18}H_{37})_4N^+$, $(C_{18}H_{27})_3(CH_3)N^+$, $(C_{18}H_{37})_2(CH_3)_2N^+$, $(C_{18}H_{37})(CH_3)_3N^+$ and $((C_{18}H_{37})_{75\%}(C_{16}H_{33})_{25\%})_2(CH_3)_2N^+$.
4. Catalyst according to claim 3, wherein Q is $(C_{16}H_{33})_4N^+$, $(C_{16}H_{33})_3(CH_3)N^+$, $(C_{16}H_{33})_2(CH_3)_2N^+$ or $(C_{16}H_{33})(CH_3)_3N^+$.
5. Catalyst according to claim 1, wherein the metal M is Mg.
6. Catalyst according to claim 1 or 5, wherein a is 1, b is 1 and c is 1.
7. Catalyst according to claim 5 or 6, wherein the catalyst is a compound of the formula $C_{16}H_{33}(CH_3)_3N^+[MgVO_4]^-$.
8. Method for the production of a catalyst according to any of claims 1 to 7, which comprises the steps of
 - a) providing a solution of a salt of the metal M in nitric acid,
 - b) adding a salt of the quaternary ammonium cation Q to the solution obtained in step a),
 - c) adding a solution of a salt of an orthovanadate to the solution obtained in step b),

- d) stirring the solution obtained in step c),
- e) concentrating the solution of step d) under reduced pressure to give a catalytically active mass, and
- f) drying the catalytically active mass obtained in step e),

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wherein the sequence of the steps b) and c) can be changed.

9. Use of a catalyst according to any of claims 1 to 7 or of a catalyst obtainable and/or obtained by a method according to claim 8 in the oxidation of sulfur containing hydrocarbon compounds.

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10. Use according to claim 9, wherein the oxidation reaction is the oxidation of alkylmercaptans to dialkyldisulfides and/or alkanesulfonic acids with oxygen or hydrogen peroxide as oxidizing agent in the presence or absence of nitric acid, or the oxidation of dialkyldisulfides to alkanesulfonic acids with oxygen or hydrogen peroxide as oxidizing agent in the presence or absence of nitric acid or the oxidation of dialkylpolysulfides to alkanesulfonic acids with oxygen or hydrogen peroxide as oxidizing agent in the presence or absence of nitric acid.

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11. Use according to claim 10, wherein the oxidation reaction is the oxidation of methylmercaptan to dimethyldisulfide and/or methanesulfonic acid with oxygen or hydrogen peroxide as oxidizing agent in the presence or absence of nitric acid or the oxidation of dimethyldisulfide to methanesulfonic acid with oxygen or hydrogen peroxide as oxidizing agent in the presence or absence of nitric acid or the oxidation of dimethylpolysulfide to methanesulfonic acid with oxygen or hydrogen peroxide as oxidizing agent in the presence or absence of nitric acid.

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- 25 12. Process for the preparation of alkanesulfonic acids comprising the steps of

- a) providing a solution comprising a sulfur containing hydrocarbon compound and a catalyst according to any of claims 1 to 7 or a catalyst obtainable and/or obtained by a method according to claim 8 in an organic solvent,

- b) introducing oxygen or hydrogen peroxide into the reaction system, and
- c) stirring the resulting mixture.

- 5 13. Process according to claim 12, wherein water, if required, is added in an amount which is sufficient to give the desired alkanesulfonic acid.
14. Process according to claim 12 or 13, wherein the sulfur containing hydrocarbon compound is methylmercaptan or dimethyldisulfide
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15. Process according to any of claims 12 to 14, wherein the organic solvent is selected from optionally substituted alkanes, preferably halogenated alkanes, optionally substituted aromatic hydrocarbons, preferably halogenated aromatic hydrocarbons, esters, ethers, ketones, alcohols, carboxylic acids, nitriles amides, sulfones, sulfoxides, alkanesulfonic acids and combinations thereof.
- 15