

**Mo containing catalyst, a preparation method and a method
for preparing methyl mercaptan**

The invention relates to a process for the preparation of a
Mo and Te containing catalyst, and the catalyst itself,
5 useful for methanethiol synthesis from syngas preferably
containing high amounts of H_2S .

THE PRIOR ART

As an important chemical educt for the production of
methionine, pesticides and medicine, methanethiol is
10 predominantly prepared by the reaction of hydrogen sulfide
with methanol. For example, US appl. 856,232 discloses a
methanethiol synthesis method based on the reaction of
hydrogen sulfide with methyl alcohol or diethyl ether; FR
appl. 93,112,491 discloses a preparation method based on
15 the reaction of methyl thio-ether with hydrogen over a
transition metal catalyst; EP167,354 discloses a synthesis
pathway with a catalyst based on titanium dioxide support
and containing NiO or MoO_3 as active components for the
reaction of hydrogen sulfide with carbon monoxide; Chinese
20 patent applications CN1207957 and CN98118187.2 disclose two
catalysts for methyl mercaptan synthesis from syngas
containing high amounts of H_2S , in which the active
component Mo-S-K is formed from the precursor of K_2MoS_4 or
 $(NH_4)_2MoS_4$ plus one potassium salt; WO 2005/040082 discloses
25 two Mo-O-K/ SiO_2 catalysts for the methanethiol synthesis,
wherein the promoters are chosen from the group consisting
of oxides of Co, Ni, Fe, Mn or La and Ce, whereby the
active component Mo-O-K is formed from K_2MoO_4 or
 $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ plus a potassium salt as precursors.

30 **STATEMENT OF THE INVENTION**

The object of this invention is the preparation of
catalysts with high activity and selectivity for the one-
step methanethiol synthesis from syngas, preferably

containing high amounts of H_2S . This means preferably a content in the range of 50 to 80 Vol.% H_2S .

DETAILED DESCRIPTION OF THE INVENTION

The catalyst according to the invention comprises active
5 components, active promoters and a support material. It is directed to a supported catalyst comprising

- a) a Mo containing and a K containing compound as active components, whereby Mo and K can be constituents of the same compound,
- 10 b) a promoter, wherein the promoter comprises TeO_2 and
- c) an oxidic carrier.

Said active component is preferably a Mo-O-K-based active center. Precursors of the Mo and K containing compounds are

- 15 a) K_2MoO_4 or
- b) $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ denoted by MoO_3 plus a potassium salt denoted as a K_2O precursor or
- c) MoO_3 plus one kind of potassium salt, said potassium
20 compound is at least one chosen from the group comprising K_2CO_3 , KOH and CH_3COOK or any other potassium containing compound being known as a K_2O precursor.

Said promoter is a Te-containing compound denoted by TeO_2 whereby H_6TeO_6 ($\text{H}_2\text{TeO}_4 \times 2 \text{H}_2\text{O}$) or any other Te-containing
25 salts or compounds being suitable as TeO_2 -precursors are used, also a potassium salt of said telluric acid H_6TeO_6 .

Said support is preferably SiO_2 or an oxidic carrier such as TiO_2 , ZrO_2 , Al_2O_3 , $\text{Al}_2\text{O}_3\text{-SiO}_2$, zeolites, pure or mixtures of said metal oxides.

For the catalyst $\text{TeO}_2\text{-K}_2\text{MoO}_4/\text{SiO}_2$ (prepared from K_2MoO_4) the weight ratio is $\text{TeO}_2/\text{K}_2\text{MoO}_4/\text{SiO}_2 = (1-20)/(1-50)/100$, more preferably $(3-12)/(15-30)/100$, for the catalyst $\text{TeO}_2\text{-MoO}_3\text{-K}_2\text{O}/\text{SiO}_2$ (prepared for example from $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and a potassium containing salt) the weight ratio is

5 $\text{TeO}_2/\text{MoO}_3/\text{K}_2\text{O}/\text{SiO}_2 = (1-20)/(1-50)/(1-50)/100$, more preferably $(3-12)/(15-30)/(8-20)/100$.

The invention is also directed to a method to prepare a catalyst according to claim 1, comprising the steps:

- 10 a) impregnating said carrier in more than one step with one or more aqueous solutions comprising a Te containing compound which acts as a TeO_2 precursor and a K containing compound which acts as a K_2O precursor and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ or MoO_3 as Mo containing compounds; or
- 15 b) impregnating said carrier in more than one step with one or more aqueous solutions comprising a Te containing compound which acts as a TeO_2 precursor and K_2MoO_4 ;
- c) drying the received impregnated carrier; and
- d) optionally treating said impregnated carrier with H_2
- 20 or syngas ($\text{CO} + \text{H}_2$) or a syngas and H_2S at elevated temperatures, preferably 200 to 450°C .

Products which are not pre-treated with said gases are also part of the invention.

The formulas of catalysts prepared are expressed as

25 $\text{TeO}_2/\text{K}_2\text{MoO}_4/\text{carrier}$ or $\text{TeO}_2/\text{MoO}_3/\text{K}_2\text{O}/\text{carrier}$.

Being exposed to a hydrogen sulphide containing atmosphere the oxidic compounds of Mo, K, Te comprised in the catalyst are converted into sulphides in complete or partially. That means that oxides or sulfides or mixtures of both are

30 contained on the catalyst carrier.

XPS-spectra of said sulfided catalysts modified by different amounts of TeO_2 show, that there are higher relative concentrations of Mo^{4+} and Mo^{5+} on the surface of the TeO_2 -promoted catalysts as compared to K_2MoO_4 /carrier (especially SiO_2), accompanied by lower concentrations of Mo^{6+} at the same time. The catalyst contains TeO_2 in the range from 5 to 20, especially 7 to 12 wt.%, based on the total weight of the catalyst.

10 In order to achieve a better distribution of the active component and the promoter on the surface of the carrier, at least one chelating reagent is preferably present in the impregnation process. Said chelating reagents are chosen from carboxylic acids such as citric acid, tri-ammonium
15 citrate, L-glutamic acid, tartaric acid and complexing agents such as ethylenediaminetetraacetic acid (EDTA), while the amount of chosen chelating agent added is 0.1-0.6 times by weight as much as that of the carrier and more preferably is 0.3-0.6 by weight. Ammonia should be added to
20 adjust the pH value of the impregnating liquor to 8-10, the preferred operating procedure is an at least two step impregnation method comprising:

(1) when K_2MoO_4 is chosen as the precursor of the active compound, a given quantity of H_6TeO_6 according to the
25 desired weight ratio is dissolved in a given quantity of distilled water to produce an aqueous solution, with which an according quantity of carrier is impregnated for 8-10 h, then dried at $100-135^\circ\text{C}$ for 4-6h to produce an intermediate product; a given quantity of at least one chelating reagent
30 and K_2MoO_4 are then dissolved in a given quantity of distilled water to produce an aqueous solution, into which a suitable amount of ammonia water is added to adjust the pH value to 8-10. The intermediate product produced above is impregnated with said solution for 8-10h, finally said

impregnated material is dried at elevated temperatures, especially at 110-135°C for 4-6h.

(2) When $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ plus one of the above-mentioned potassium compounds are chosen as the precursors of the active compound, the order of preparation is preferably as follows: first) a quantity of chosen potassium compound and a given quantity of H_6TeO_6 according to the desired weight ratio of Mo and Te are dissolved in a given quantity of distilled water to generate an aqueous solution. An according quantity of carrier is impregnated with said solution for 8-10h, then dried at elevated temperatures, especially at 100-130°C for 4-6h to form a $\text{H}_6\text{TeO}_6\text{-K/SiO}_2$ intermediate product; a quantity of a chosen chelating reagent and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ are then dissolved in a prescribed amount of distilled water to produce an aqueous solution, the pH value of which is adjusted to 8-10, by adding a suitable amount of ammonia water. Said intermediate product is then impregnated with said solution for 8-10h, followed by drying it at elevated temperatures, especially at 110-135°C for 4-6h.

It is also possible to change the step sequence:

(3) A given quantity of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and a given quantity of H_6TeO_6 are dissolved in a given quantity of distilled water to generate an aqueous solution. A given quantity of SiO_2 is impregnated for 8-10h, with said solution then dried at elevated temperatures, especially at 100-130°C for 4-6h to form a Mo-O-Te/SiO_2 intermediate product; a given quantity of potassium compound is dissolved in a given quantity of distilled water to produce an aqueous solution, into which a given quantity of the chosen chelating agent and ammonia water are added to adjust the pH value of the solution to 8-10, with which the Mo-O-Te/SiO_2 produced above is impregnated for 8-10h, followed by drying at 110-135°C for 4-6h.

A continuous process for the manufacture of methyl mercaptan is successfully carried out by reacting a mixture of carbon oxides, sulphur or hydrogen sulphide and hydrogen at elevated temperatures and pressures in the presence of
5 the above described catalysts.

The feed gas has preferable a hydrogen sulphide content in the range of 50 - 80 Vol.%.

It is preferred to feed the reactants carbon oxide, sulphur, hydrogen sulphide and hydrogen to the reactor in a
10 molar ratio from 1/0/1/0 to 1/10/10/10, preferably from 1/0/2/2 to 1/0/10/10.

The reaction conditions as well as purification of the product and the recycling of non reacted compounds are generally known (US 4,665,245 / EP-A-104507; WO
15 2005/040082).

The catalyst should be pretreated with H₂ or syngas (CO+H₂) for 8-10h preferably followed by sulfiding with H₂S prior to the catalytic conversion of carbon monoxide, hydrogen and hydrogen sulphide to methanethiol to obtain the TeO₂
20 component of the promoter.

The evaluation of the catalytic performance of the catalyst in the present invention was carried out in a fixed-bed tubular reactor with 0.5ml of catalyst per pass. The experiments were performed under the reaction conditions of
25 CO/H₂/H₂S=1/1/2, 300°C, 0.2MPa and GHSV = 2000h⁻¹. The products were analyzed by GC. All data were obtained after steady state conditions were achieved.

The following examples illustrate the present invention.

EXAMPLE 1

30 Under stirring 0.648g of H₆TeO₆ were fully dissolved in 10.0ml of distilled water, the pH value of the aqueous

solution of H_6TeO_6 thus prepared was measured to be 4.1, then 5.000g of SiO_2 were impregnated with the aqueous solution of H_6TeO_6 at room temperature for 8h, followed by drying at 120°C for 5h to produce a dried intermediate product.

Under stirring 2.068g of K_2MoO_4 were fully dissolved in 5.0 ml of distilled water to produce a K_2MoO_4 aqueous solution, into which 5ml of $\text{NH}_3\cdot\text{H}_2\text{O}$ were added, the pH value of the aqueous solution was measured to be 11.40, then, under stirring 3.000g of citric acid were added to the aqueous solution of K_2MoO_4 plus $\text{NH}_3\cdot\text{H}_2\text{O}$, the pH value of the K_2MoO_4 plus $\text{NH}_3\cdot\text{H}_2\text{O}$ solution was measured to be 9.26. Finally, the intermediate product prepared in step (1) was impregnated with the solution containing citric acid K_2MoO_4 plus $\text{NH}_3\cdot\text{H}_2\text{O}$ at room temperature for 10h, followed by drying at 120°C for 5h to generate a catalyst comprising $\text{TeO}_2/\text{K}_2\text{MoO}_4/\text{SiO}_2$, showing the weight ratio of 9/25/100. The evaluation results of the catalyst thus prepared are shown in table 1.

EXAMPLE 2

(1) Under fast stirring, 1.468g of K_2CO_3 and 0.648g of H_6TeO_6 were fully dissolved in 10ml of distilled water to form an aqueous solution, with which 5.000g of SiO_2 were impregnated at room temperature for 9h, and finally dried at 125°C for 4h to generate an intermediate product.

(2) 1.534g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ were fully dissolved in 5.0 ml of distilled water under agitating to form an aqueous solution, to which 2.000g of tri-ammonium citrate were added. Subsequently, a suitable amount of $\text{NH}_3\cdot\text{H}_2\text{O}$ was added to adjust the pH of the solution to 9.05. The intermediate product prepared in step (1) was impregnated with said solution at room temperature for 9h and finally dried at 125°C for 4h to produce the catalyst $\text{K}_2\text{O}/\text{MoO}_3/\text{TeO}_2/\text{SiO}_2$, showing the weight ratio of 20/25/9/100. The evaluation results of the catalyst thus prepared are shown in table 1.

EXAMPLE 3

The catalyst was prepared according to the method described
5 in Example 1, but 2.000g of tartaric acid was used as
chelating reagent and the carrier SiO_2 was replaced by γ -
 Al_2O_3 . The evaluation results of the catalyst thus prepared
are shown in table 1.

EXAMPLE 4 AND 5

10 The catalyst was prepared according to the method described
in Example 1, but the quantity of H_6TeO_6 was changed to be
0.486g and 0.432g respectively, and the chelating reagents
used was EDTA in both cases, the weight ratio of the final
catalysts thus prepared were $\text{TeO}_2/\text{K}_2\text{MoO}_4/\text{SiO}_2 = 6.75/25/100$
15 and $\text{TeO}_2/\text{K}_2\text{MoO}_4/\text{SiO}_2 = 6/25/100$ respectively. The
evaluation results of the catalysts thus prepared are shown
in table 1.

EXAMPLE 6

The catalyst was prepared according to the method described
20 in Example 1, but 5.000g of TiO_2 was used as the carrier.
The amount of H_6TeO_6 and the amount of K_2MoO_4 were replaced
by 0.142g and 0.827g, respectively. The final catalyst
prepared was $\text{TeO}_2/\text{K}_2\text{MoO}_4/\text{TiO}_2 = 2/10/100$. The evaluation
results of the catalyst thus prepared are shown in table 1.

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EXAMPLE 7

The catalyst was prepared according to the method described
in Example 6, but 5.000g of ZrO_2 was used as the carrier.
and the amount of H_6TeO_6 and K_2MoO_4 was replaced by 0.071g
30 and 0.414g respectively. The final catalyst prepared was

$\text{TeO}_2/\text{K}_2\text{MoO}_4/\text{ZrO}_2=1/5/100$. The evaluation results of the catalyst thus prepared are shown in table 1.

5 **EXAMPLE 8**

The catalyst was prepared according to the method described in Example 2, but 5.000g of the mesoporous molecular sieve MCM-41 was used as the carrier, and the amount of K_2CO_3 , H_6TeO_6 and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ was replaced by 1.835g, 1.080g
10 and 2.454g, respectively. The final catalyst prepared was $\text{K}_2\text{O}/\text{MoO}_3/\text{TeO}_2/\text{MCM-41} = 25/40/15/100$.

The evaluation results of the catalysts modified with different amounts of TeO_2 for methanethiol synthesis from
15 high H_2S containing feed gas are listed in table 1.

As it can be seen the addition of TeO_2 to $\text{K}_2\text{MoO}_4/\text{SiO}_2$ catalyst increases evidently the activity of the catalysts, which can find expression in the significant change of
20 conversion of CO and the yield of CH_3SH . The conversion of CO reaches a maximum with 61,5% and a yield of methanethiol of $0,39 \text{ g.ml}_{\text{cat}}^{-1}.\text{h}^{-1}$. Obviously, both the conversion of CO and the yield of methanethiol do not correspond linearly or regularly as function of the amount of TeO_2 added.

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Table 1 The evaluation results of the catalysts in examples 1-8.

Example (catalyst)	Selectivity (%)				CO ₂ / CH ₃ SH	Yield (g. ml _{cat} ⁻¹ . h ⁻¹)				Conv. Of CO (%)
	CH ₄	CH ₃ SH	COS	CO ₂		CH ₄	CH ₃ SH	COS	CO ₂	
1, K ₂ MoO ₄ /TeO ₂ /SiO ₂ = 25/9/100	0.23	55.21	10.70	33.86	0.61	0.0005	0.38	0.09	0.21	59.29
2, K ₂ O/MoO ₃ / TeO ₂ /SiO ₂ = 15/25/9/100	0.25	55.15	11.30	33.30	0.60	0.0005	0.35	0.09	0.19	57.26
3, K ₂ MoO ₄ /TeO ₂ /γ -Al ₂ O ₃ = 25/9/100	0.30	48.70	17.91	33.08	0.68	0.0005	0.24	0.09	0.21	56.02
4, K ₂ MoO ₄ /TeO ₂ /SiO ₂ = 25/6.75/100	0.24	54.74	10.72	34.90	0.60	0.0005	0.35	0.09	0.21	56.02
5, K ₂ MoO ₄ /TeO ₂ /SiO ₂ = 25/6/100	0.24	54.50	10.50	35.02	0.66	0.0005	0.36	0.09	0.22	57.52

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6, K ₂ MoO ₄ /TeO ₂ /TiO ₂ =10/2/100	0.08	48.40	14.05	37.47	0.77	0.0005	0.31	0.09	0.24	48.4
7, K ₂ MoO ₄ /TeO ₂ /ZrO ₂ =5/1/100	0.09	48.17	17.84	33.90	0.70	0.0005	0.27	0.10	0.19	39.6
8, K ₂ O/MoO ₃ /TeO ₂ / MCM-41 =25/40/15/100	0.07	51.28	11.83	36.82	0.72	0.0005	0.39	0.09	0.28	61.5

EXAMPLE 9

Figure 1 shows X-ray diffractograms of the catalyst $\text{TeO}_2\text{-K}_2\text{MoO}_4/\text{SiO}_2$ prepared by drying of the catalyst at 150°C and calcination at 400°C as compared to the starting materials
5 and the catalysts $\text{K}_2\text{MoO}_4/\text{SiO}_2$ and $\text{CoO-K}_2\text{MoO}_4/\text{SiO}_2$ [A) carrier SiO_2 ; B) H_6TeO_6 ; C) $\text{K}_2\text{MoO}_4/\text{SiO}_2$; D) $\text{TeO}_2\text{-K}_2\text{MoO}_4/\text{SiO}_2$ (prepared with citric acid; drying at 150°C); E) $\text{TeO}_2\text{-K}_2\text{MoO}_4/\text{SiO}_2$ (prepared with HNO_3 and without chelating
10 reagent); F) $\text{CoO-K}_2\text{MoO}_4/\text{SiO}_2$; G) $\text{TeO}_2\text{-K}_2\text{MoO}_4/\text{SiO}_2$ (calcined at 400°C); H) $\text{CoO-K}_2\text{MoO}_4/\text{SiO}_2$ (calcined at 500°C)]. The diffractograms clearly demonstrate the distinct nature of the Te-containing catalysts as compared to other catalysts prepared on the basis of the system $\text{K}_2\text{MoO}_4/\text{SiO}_2$

Claims

1. A supported catalyst comprising
 - a) a Mo and a K compound as active components, whereby Mo and K can be constituents of the same compound,
 - 5 b) a promoter, wherein the promoter comprises TeO_2 and and
 - c) an oxidic carrier
2. The catalyst according to claim 1, wherein the weight ratios of the components are
 - 10 $\text{TeO}_2/\text{KMoO}_4/\text{carrier} = (1-20)/(1-50)/100$ or
 - $\text{TeO}_2/\text{MoO}_3/\text{K}_2\text{O}/\text{carrier} = (1-20)/(1-50)/(1-50)/100$.
3. The catalyst according to claim 2, wherein the weight ratios of the components are
 - (1) $\text{TeO}_2/\text{KMoO}_4/\text{carrier} = (3-12)/(15-30)/100$ or
 - 15 (2) $\text{TeO}_2/\text{MoO}_3/\text{K}_2\text{O}/\text{carrier} = (3-12)/(15-30)/(8-20)/100$
4. The catalyst according to claim 1, wherein the carrier is chosen from the group comprising SiO_2 , Al_2O_3 , TiO_2 , $\text{Al}_2\text{O}_3\text{-SiO}_2$, ZrO_2 , zeolites, carbon containing materials or mixtures thereof.
- 20 5. The catalyst according to claim 1, wherein the catalyst contains an active Mo-O-K center.
6. The catalyst according to claims 1 to 5, wherein the catalyst is sulfided by exposing to an hydrogen sulphide containing atmosphere.
- 25 7. The catalyst according to claims 1 to 6, wherein the TeO_2 content is in the range from 1 to 20 wt.%.

8. A method to prepare a catalyst according to claims 1 to 7, comprising the steps:

5 a) impregnating said carrier in more than one step with one or more aqueous solutions comprising a Te containing compound which acts as a TeO_2 precursor and a K containing compound which acts as a K_2O precursor and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ or MoO_3 as Mo containing compounds; or

10 b) impregnating said carrier in more than one step with one or more aqueous solutions comprising a Te containing compound which acts as a TeO_2 precursor and K_2MoO_4 ;

9. A method according to claim 8, comprising the steps:

15 a1) impregnating the carrier with an aqueous solution of a Te-containing compound which is a TeO_2 precursor, drying said impregnated carrier at elevated temperatures to produce an intermediate product (a).

20 a2) impregnating said product (a) with an aqueous solution of K_2MoO_4 to produce a product (b) with weight ratios of the components according to ratio (1) and drying the said product (b) at elevated temperatures; or

25 b1) impregnating the carrier with an aqueous solution of a Te-containing compound which is a TeO_2 precursor and of a K-containing compound which is a K_2O precursor, drying said impregnated carrier at elevated temperatures to produce an intermediate product (c); and

30 b2) impregnating said intermediate product (c) with an aqueous solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ to produce a catalyst with weight ratios of the components

according to ratio (2) and drying said impregnated product (d),

whereby the pH-value during the second impregnation steps a2) and b2) is adjusted to a range of 8 to 10.

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10. The method according to claim 9, whereby adjusting the pH value is achieved by adding a suitable amount of ammonia water or ammonia.

11. The method according to claim 9, whereby at least one chelating reagent is added during impregnation with the Mo containing compound.

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12. The method according to claim 9 and 11, whereby the chelating reagent is added in a weight of 0,1 to 0,6/1 relative to the carrier.

13. The method according to claims 9 to 12, whereby the chelating reagent is chosen from the group of citric acid, tri ammonium citrate, L-glutamic and tartaric acid or ethylenediaminetetraacetic acid (EDTA).

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14. The method according to claims 8 to 13, whereby the catalyst is sulfided by exposing to a hydrogen sulphide containing atmosphere.

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15. A method for preparing methyl mercaptan in a catalytic process by reacting carbon oxides, such as CO, CO₂, or mixtures thereof, sulphur and/or hydrogen sulphide, and hydrogen, whereby the reaction takes place in the presence of a supported catalyst comprising

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a) a Mo and a K compound as active components, whereby Mo and K can be constituents of the same compound,

b) a promoter, wherein the promoter comprises TeO₂

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c) an oxidic carrier.

16. The method of claim 15, wherein the weight ratios of the components are

$\text{TeO}_2/\text{K}_2\text{MoO}_4/\text{Carrier} = (3-12)/(15-30)/100$ or

5 $\text{TeO}_2/\text{MoO}_3/\text{K}_2\text{O}/\text{carrier} = (3-12)/(15-30)/(8-20)/100.$

17. The method of claim 15 wherein the carrier is chosen from the group, comprising SiO_2 , TiO_2 , Al_2O_3 , $\text{Al}_2\text{O}_3\text{-SiO}_2$, zeolites, carbon containing materials or mixtures thereof.

10 18. The method of claims 15 to 17, wherein the reactants carbon oxides, such as CO, CO_2 , or mixtures thereof, sulphur, hydrogen sulphide and hydrogen are fed to the reaction in a molar ratio from 1:0:1:0 to 1:10:10:10.

15 19. The method of claims 15 to 17, wherein the molar ratio of the reactants carbon oxides, such as CO, CO_2 , or mixtures thereof, sulphur, hydrogen sulfide and hydrogen reach from 1:0:2:2 to 1:0:10:10.