

Methanol oxidation catalyst

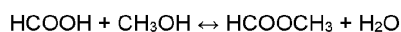
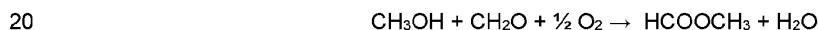
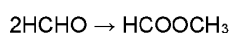
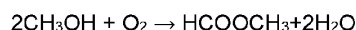
Field of the Invention

The present invention concerns a catalyst composition for the oxidation of methanol to produce formaldehyde. In particular, a catalyst composition which reduces the undesirable by-product methyl formate.

Background

Processes for the manufacture of formaldehyde in which methanol is oxidised over a catalyst have been well-known for many years. One well-known process includes the oxidation of methanol over a mixed oxide catalyst, usually containing oxides of iron and molybdenum: $\text{CH}_3\text{OH} + 0.5 \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O}$. Plants operating this process usually operate at a reactor inlet pressure of about 1 barg or less. A further increase in pressure can result in problems due to a loss in selectivity of the catalyst. The result is an increase in formation of unwanted by-products such as carbon monoxide, dimethyl ether and methyl formate. As a consequence, the utilisation of added feedstock is decreased leading to higher operating costs than if no by-product were formed. Considering that the methanol contribution to the overall operating costs corresponds to >90%, it is highly desirable to minimise these losses.

Methyl formate can be formed according to the reactions:



It would be desirable to reduce the methyl formate because this also reduces the formaldehyde yield and profitability of the operator and leads to the production of formic acid, according to the equilibrium reaction above. Formic acid is problematic, for example, for producers of adhesives and urea formaldehyde and necessitates the addition of buffers to the formalin solution.

The present invention seeks to overcome one or more of the above disadvantages of the prior art. In particular, the present invention seeks to reduce the methyl formate loss in processes for the production of formaldehyde.

Summary of the Invention

Accordingly, the present invention provides a catalyst composition comprising:

i) a catalytic material comprising iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3); and

ii) a metal oxide A, wherein the metal oxide A is an alkaline earth metal oxide or zirconium oxide or a combination of zirconium oxide and cerium oxide.

In particular, the present invention provides a catalyst composition according to the invention comprising:

5 i) granules of the catalytic material comprising iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3); and

ii) the metal oxide A;

wherein the catalyst composition comprises a physical blend of the catalytic material comprising iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3) and the metal oxide A; and

10 wherein at least some of the metal oxide A forms a coating around the granules of the catalytic material comprising iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3).

Such catalyst compositions advantageously facilitate the oxidation of methanol to formaldehyde with reduced methyl formate selectivity and without a significant drop in methanol conversion.

15 The present invention also provides a pellet comprising the catalyst composition of the invention. Such pellets retain hardness at relatively low densities i.e. they demonstrate an improved hardness to density ratio. Lower density tablets are more active in methanol oxidation and more selective. For example, over oxidation of formaldehyde is reduced therefore less carbon monoxide is formed. However, tablets with a relatively low density are conventionally less durable. The pellets of the invention address this problem.

The present invention also provides a process for the preparation of a catalyst composition according to the invention, the process comprising the steps of:

20 i) calcining a metal oxide A to provide calcined metal oxide A;

ii) mixing the calcined metal oxide A with a catalytic material comprising iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3);

iii) calcining the mixture to provide the catalyst composition.

25 The present invention also provides a process for the preparation of a catalyst composition of the invention, the process comprising the steps of:

i) calcining a metal oxide A to provide calcined metal oxide A;

ii) calcining a catalytic material comprising iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3);

30 ii) mixing the calcined metal oxide A with the calcined catalytic material comprising iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3).

The present invention also provides a process for the production of formaldehyde from methanol comprising the steps of: feeding to a reactor a feed stream comprising the methanol and an oxygen-containing gas; reacting the methanol in the gas phase with the oxygen-containing gas in the reactor in the presence of a catalyst composition or tablet according to the invention.

- 5 The present invention also provides use of a catalyst composition of the invention, to reduce methyl formate loss in a process for the production of formaldehyde from methanol.

Brief Description of the Drawings

Figure 1 is a chart showing methyl formate selectivity against methanol conversion for catalyst compositions according to the invention and a comparative catalyst.

- 10 **Figure 2** is a chart showing methyl formate selectivity against methanol conversion for further catalyst compositions according to the invention and a comparative catalyst.

Figure 3 is a chart showing methyl formate selectivity against methanol conversion for further catalyst compositions according to the invention and a comparative catalyst.

- 15 **Figure 4** is a chart showing methyl formate selectivity against methanol conversion for further catalyst compositions according to the invention and a comparative catalyst.

Figure 5 is a chart showing density against hardness for pellets containing catalyst compositions according to the invention.

Figure 6 is a TEM image of catalyst composition according to the invention.

Figure 7 is a collection of EDS images of catalyst composition according to the invention.

20 Detailed Description of the Invention

The catalyst composition of the invention comprises a catalytic material which is a mixture of iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3), typically having a Mo:Fe ratio between 2 and 3. Suitable catalytic materials have a surface area in the range of and including 2 to 20 m^2/g , for example 3 to 10 m^2/g . The catalytic material comprising iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (25 MoO_3) may optionally contain copper, for example as described in WO2022/079434 and/or oxides of other metals such as vanadium, aluminium, silicon, calcium, cobalt, chromium, magnesium, manganese, nickel, zinc, silver and titanium. As a skilled person will understand, such additional components will be present in a minor amount, such as no more than about 1.0 wt%, typically no more than 0.5 wt%.

- 30 The catalyst composition of the invention also comprises a metal oxide A, wherein the metal oxide A is an alkaline earth metal oxide or zirconium oxide or a combination of zirconium oxide and cerium oxide. In one aspect, the metal oxide A is an alkaline earth metal oxide. A preferred alkali metal earth oxide is magnesium oxide. In one aspect, the metal oxide A is zirconium oxide. In another aspect, the metal oxide

A is a combination of zirconium oxide and cerium oxide, for example in a weight ratio in the range of and including 5:1 to 1:5, typically in a weight ratio of about 1:1.

Typically, the catalytic material comprising iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3) is in the form of granules, suitably arising from an agglomeration of particles of the catalytic material.

- 5 Suitably, the catalyst composition is a physical blend of the catalytic material comprising iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3), and the metal oxide A. For example, discrete solid forms of the catalytic material and the metal oxide A exist in the catalyst composition. Suitably, at least some of the metal oxide A forms a coating around the granules of the catalytic material comprising iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3). For example, the discrete solid form of metal oxide A is
- 10 distributed, typically homogeneously, over substantially all of the surface of the granules of catalytic material and bound or fixed to the granules by physical or chemical bonds. Put another way, the catalyst composition comprises granules of the catalytic material comprising iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3) which are dry coated, suitably with a homogenous coating, with the metal oxide A. Typically, at least about 50% by weight of the metal oxide A forms a coating around the granules
- 15 of the catalytic material comprising iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3).

- Typically, the metal oxide A may present in an amount of no more than about 15 wt% by total weight of the catalyst composition, preferably no more than about 5 wt% by total weight of the catalyst composition, more preferably no more than about 3 wt% by total weight of the catalyst composition, even more preferably no more than about 2 wt% by total weight of the catalyst composition. The metal oxide A is
- 20 typically present in an amount of at least about 0.1 wt% by total weight of the catalyst composition.

- The catalyst composition may further comprise an alkali metal, suitably sodium. Preferably, the metal oxide A is impregnated with the alkali metal. The alkali metal is suitably present in an amount of no more than about 5 wt% by weight of the metal oxide A, preferably no more than about 1 wt% by weight of the metal oxide A, more preferably no more than about 0.5 wt% by weight of the metal oxide A. The alkali
- 25 metal is typically present in an amount of at least about 0.1 wt% by total weight of the catalyst composition.

- To prepare the catalyst composition, the catalytic material comprising iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3) is first typically sieved to give a particle size in the range of and including about 200 to about 400 μm , as measured by sieving. In one aspect, the catalytic material comprising iron
- 30 molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3) is then calcined at a temperature typically in the range of and including about 400 to about 550°C before mixing with the metal oxide A. In this aspect, there is typically no step of calcination after the step of mixing of the catalytic material comprising iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3) and the metal oxide A. In an alternative aspect, the catalytic material comprising iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3) is not
- 35 calcined prior to mixing with the metal oxide A. In this alternative aspect, it is a requirement that calcination is carried out after mixing of the catalytic material comprising iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3) and the metal oxide A. Such a calcination may be carried out at a temperature in the range of and including about 400 to about 550°C, typically for a time of less than about 120 hours. In the case of all of the calcination steps discussed herein, the calcination time is not

particularly limited and calcination is carried out for as long as is needed for the desired surface area of the material. The overall time will depend on factors such as the furnace used, flow conditions and heat transfer and a skilled person using common general knowledge can determine the time needed. As demonstrated in the Examples section, both synthetic methods provide catalyst compositions which

5 typically comprise the catalytic material comprising iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3) dry coated with the metal oxide A, and which achieve the benefit of the invention. Metal oxide A is calcined before mixing with the catalytic material comprising iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3), in any aspect. Such calcination may be carried out at a temperature in the range of and including about 300 to about 1200°C typically for a time of less than about 120 hours. The

10 mixing of the catalytic material comprising iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3) and the metal oxide A can be any form of physical mixing, typically blending of the two solid forms for example by hand or using automated means such as resonance acoustic mixing. Suitably, the metal oxide A has a particle size, measured by sieving, which is smaller than the granules, as measured by sieving, of the catalytic material comprising iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide

15 (MoO_3). As demonstrated in the Examples section, the particular method used for blending is not particularly limited which is a benefit of the catalyst composition. When the catalyst composition comprises an alkali metal it is preferably the metal oxide A which is impregnated with the alkali metal. This is typically achieved by precipitation of the alkali metal from a solution, typically aqueous, of a soluble alkali metal salt in the presence of metal oxide A which has not undergone calcination. This may

20 be carried out by adding the solution dropwise to the metal oxide A prior to a step of heating, for example in the range of and including about 80 to about 120 °C. For an even distribution of alkali metal, the soluble alkali metal salt may be dissolved in enough solvent, typically water, to fill the pores of the metal oxide A without overfilling. A skilled person can determine such an amount using common general knowledge. The impregnated metal oxide A is then calcined at a temperature in the range of and including about 300

25 to about 1200°C typically for a time of less than about 120 hours. The alkali metal salt may, for example, be a hydroxide salt or a chloride salt.

The catalyst composition of the invention may be incorporated into a formed or extruded catalyst. Accordingly, provided herein is a formed or extruded catalyst comprising the catalyst composition of the invention. The catalyst composition may be formed into a pellet, preferably a ring-shaped pellet.

30 Accordingly, provided herein is a pellet comprising the catalyst composition of the invention, preferably a ring-shaped pellet. The size of such a pellet will depend on a particular application. Suitably, ring-shaped pellets have an outer diameter in the range of and including about 4.5 to about 5.5 mm. Suitably, ring-shaped pellets have an inner diameter in the range of and including about 2.0 to about 3.7 mm. Suitably, ring-shaped pellets have a height in the range of and including about 2.0 to about 5.5 mm. Pellets can be

35 formed using standard means known to a skilled person and the process may include the use of additives such as lubricants, i.e. graphite, and pore forming agents. Generally, such additives will be removed during subsequent heating steps. However, for example, some lubricant may remain in the formed pellet in amounts of less than about 1 wt%. A heating step is performed after the step of forming pellets. In the process for the preparation of a catalyst composition of the invention in which there is a step iii) of

40 calcining the mixture to provide the catalyst composition, the step of forming pellets is performed before

this step iii) and as such the calcination step provides the required heat. The pellets suitably have a hardness, typically in the axial direction, to density ratio of greater than 9, typically greater than 10. Hardness to density ratio being hardness (kP)/density (g/cm^3). The pellets suitably have a hardness in the axial direction of at least about 7 kP, typically at least about 20 kP. The pellets typically have a hardness
5 in the axial direction of at most about 40 kP. Hardness is measured in the axial direction on a ring-shaped pellet having a 5.0 mm outer diameter, an inner diameter of 2.75 mm and a height of 2.5 mm by a Sotax MultiTest 50-FT WTDH 800N 100-240V/50-60Hz or any equivalent instrument. The pellets also suitably have a density of at most about $2.2 \text{ g}/\text{cm}^3$, typically at most about $2.0 \text{ g}/\text{cm}^3$, more typically less than about $1.9 \text{ g}/\text{cm}^3$. The pellets typically have a density of at least about $1.5 \text{ g}/\text{cm}^3$. Tablet density is
10 calculated using the average mass and volume of 10 tablets at ambient temperature and pressure e.g. 25°C and 1 atm. Dimensions for volume can, for example, be measured using an optical microscope.

Typical processes for the production of formaldehyde from methanol are known, for example, from WO96/32189 and US2,504,402. A well-known process for the production of formaldehyde is the Formox process offered by Johnson Matthey for example as described in WO2022/079434.

15 In the process for preparing formaldehyde from methanol, the reactor may be operated at an inlet pressure suitable to the particular process and the plant equipment available. The skilled person must select an appropriate reactor pressure based on the plant and the desired outcome. A typical process plant for formaldehyde production using a catalytic material comprising iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3) may be operated at a reactor inlet pressure of about 0 barg. Barg indicates
20 gauge pressure in bar, i.e. the pressure above atmospheric pressure. Barg may be converted to bar absolute (bara) by adding the local atmospheric pressure in bar. Using the process of the invention the reactor inlet pressure may be at least 0.4 barg. It is a particular benefit of the process of the invention that the reactor inlet pressure may be increased without increasing, or even while still reducing, the methyl formate loss. In other words, because the invention reduces methyl formate loss compared to prior art
25 processes at the same pressure, a prior art process can have the invention applied and the pressure increased and still maintain the same or better methyl formate loss and/or methyl formate loss. Therefore, the reactor inlet pressure may preferably be at least about 0.4 barg, more preferably at least about 1.0 barg, yet more preferably greater than about 1.5 barg, and even more preferably greater than about 3 barg. The reactor inlet pressure may be up to about 10 barg or higher than about 10 barg.

30 The oxygen-containing gas may be any suitable gas stream. The concentration of oxygen in the reactor is usually selected by the process designer according to the process which is intended. For example, the oxygen concentration may be selected so that the mixture of oxygen and organic compounds is not explosive. In a typical formaldehyde-producing process, the oxygen-containing gas is air. The oxygen-containing gas may be mixed with the methanol and other components of the feed stream, such as a
35 recycled stream, either within the reactor, at the reactor inlet or before the feed stream is fed through the reactor inlet.

The feed stream may comprise methanol at a concentration of from 1% to 20% by volume of said feed stream. The feed stream may comprise from 3% to 15% by volume of methanol, for example from about 6 vol% to about 12 vol%.

- In a typical process the reaction products which leave the reactor which contain some of the product formaldehyde are treated to remove a portion of the product formaldehyde from the formaldehyde reactor outlet stream. This creates a formaldehyde product stream comprising the removed formaldehyde product and a treated stream comprising some formaldehyde along with other by-products such as the carbon monoxide as well as, usually, unreacted methanol, water and dimethyl ether. The other by-products may also comprise nitrogen, for example if the oxygen-containing gas used is air. A portion of the treated stream may be recycled to the reactor. In such a case, the feed stream to the reactor may contain dimethyl ether made as a by-product in the reactor. It is known that when dimethyl ether is added to the reactor, the amount of dimethyl ether made in the reaction tends to be less. The feed stream may for example contain up to about 0.7 vol% of dimethyl ether. Typically the feed stream may contain from about 0.1 to about 0.6 vol% of dimethyl ether. Conversion of methanol to dimethyl ether is a known problem which affects the productivity of formaldehyde processes, particularly when operated at higher inlet pressures. The presence of water in the feed stream to the reactor may reduce the amount of dimethyl ether which is formed. The water may be added as described in WO2016/177999. Preferably sufficient water is added to the feed stream to bring the amount of water in the feed stream to a value in the range of from about 3.0 to about 15.0 vol% of water, preferably about 3.5 to about 10.0 vol%.
- The reaction temperature of the reacting of the methanol in the gas phase with the oxygen-containing gas in the reactor is typically greater than about 250°C, normally between about 250°C and about 400°C. The reactor feed inlet temperature may typically range from about 60°C to about 220°C. The reaction temperature may vary along the length of the reactor bed. Normally the reactor is operated such that the temperature is at a maximum at a location between the inlet and the outlet parts of the reactor. The reaction temperature in different parts of the reactor may be affected by the composition of catalyst in the catalyst bed. A mixed catalyst bed may be used, in which a catalyst may be mixed with an inert material or with a catalyst of a different composition and activity to provide a desired activity profile across the catalyst bed. In particular, the catalyst composition of the invention may be used in only part of the reactor. The reactor may comprise a catalyst bed, such as in a fixed bed reactor. The reactor will more usually comprise a plurality of parallel catalyst beds, such as in a tubular reactor where a multiplicity of tubes, each containing a catalyst bed, are surrounded by a heat transfer fluid. A tubular reactor may typically comprise hundreds or thousands of such tubes. Preferably, the downstream third of the catalyst bed or beds may comprise the catalyst composition of the invention. The downstream half of the catalyst bed or beds may comprise the catalyst composition of the invention. The catalyst composition of the invention may be used in the downstream parts of the catalyst bed or beds as that is where most methyl formate is formed. The catalyst composition of the invention may be used throughout the catalyst bed or beds or in an upstream part of the catalyst bed or beds. Using the catalyst composition of the invention in only part of the catalyst bed or beds may be particularly advantageous if the activity of the catalyst composition of the invention differs from the activity of the standard prior art catalysts.

The reaction temperature may be controlled by means of a heat transfer system. The reactor temperature may be varied over time. A typical catalyst tends to lose activity over its useful lifetime. The reactor temperature may be varied to take account of such a loss in activity.

Examples

5 Example 1

Commercial MgO (Sigma-Aldrich, 325 mesh) was calcined, using a static oven with a ramp of 5°C/min, typically up to 600°C or 1000°C, and kept at target temperature for 2 hours. An amorphous methanol oxidation catalyst comprising iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3) (Mo-Fe catalyst), as described in *Topics in Catalysis*, 50, 2008, pp 145 to 155, was sieved to a particle size in the range of 250-355 µm. The Mo-Fe catalyst (14.85g) was added to a reaction pot and the calcined MgO was added (0.15 g). This aimed at a final product comprising 99wt% Mo-Fe catalyst and 1wt% MgO. The reaction pot was then subjected to Resonance Acoustic Mixing (RAM) using a LabRAM II instrument for 5 minutes at a force of 80g. The samples were subsequently calcined at a temperature in the range of 400 to 500 °C to obtain the final catalyst. Two catalyst compositions were prepared following this method:

15 1a – which contained 1wt% of MgO that had previously been calcined at 600°C.

1b – which contained 1wt% of MgO that had previously been calcined at 1000°C.

Methyl formate selectivity % vs. methanol conversion % was evaluated for 1a and 1b, along with a reference methanol oxidation catalyst comprising iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3) as described in *Topics in Catalysis*, 50, 2008, pp 145 to 155 – C1.

20 The evaluation was carried out in a micro-reactor at 330°C, 0.5 barg and total gas flow 400 Nml/min; the oxygen, methanol, methyl formate, dimethyl ether, formaldehyde, water, and nitrogen concentrations were 7.0, 1.4, 0.2, 0.26, 4.06, 10.0, and 77.08 vol%, respectively. The weight of the C1 catalyst used in the micro-reactor was 0.1, 0.15, 0.2 and 0.25 g in separate experiments, which gave the respectively increasing levels of conversion shown in Fig. 1. The weight of the catalysts compositions 1a and 1b used
25 in the micro-reactor test was 0.2 g. Fig. 1 shows that, for 0.2 g catalyst, the methyl formate selectivity was reduced, whilst methanol conversion did not drop significantly. It can be extrapolated that this effect would also be seen at higher catalyst loading and methanol conversion.

Example 2

30 Three series of catalyst compositions were prepared to study the effect of different variables on the selectivity reduction of methyl formate. The factors investigated consisted of MgO loading, effect of the addition of Na to MgO, and the method of mixing Mo-Fe catalyst with MgO (with or without the addition of Na).

Variation of MgO loading on Mo-Fe catalyst and RAM mixing of components

Firstly, commercial MgO (Sigma-Aldrich, 325 mesh) was calcined, using a static oven with a ramp of 5°C/min, to 1000°C, and kept at target temperature for 2 hours. An amorphous Mo-Fe catalyst was sieved to a particle size in the range of 250-355 µm. The final calcined catalyst compositions were prepared following the same methodology described in Example 1. The table below shows the amounts of reactants used for each catalyst composition in this series:

	wt% MgO	MgO (g)	Mo-Fe catalyst (g)
2a	2	0.3	14.7
2b	3	0.45	14.55
2c	4	0.6	14.4
2d	5	0.75	14.25

Table 1

Variation of Na impregnated MgO loading on Mo-Fe catalyst and RAM mixing of components

Firstly, commercial MgO (Sigma-Aldrich, 325 mesh) was calcined, using a static oven with a ramp of 5°C/min, to 1000°C, and kept at target temperature for 2 hours. Subsequently, NaCl was dissolved in enough demineralised water to fill the pores of the MgO without overfilling for an even distribution of NaCl. The amount of solution required per gram of calcined MgO was 0.60 g/ml. In a glass beaker, 9.98 g of calcined MgO was weighted. In a separate beaker, 0.05 g of NaCl was weighted and dissolved in 6 ml of water. The NaCl solution was added drop wise to the calcined MgO and stirred to ensure good distribution. Then the resulting mixture was dried in an oven at 105°C for ca. 16 hours.

An amorphous Mo-Fe catalyst was sieved to a particle size in the range of 250-355 µm. The final calcined catalyst composition containing Fe-Mo catalyst and MgO impregnated with Na were prepared following the same methodology described in Example 1. The table below shows the amounts of reactants used for each sample in this series:

	wt% MgO impregnated with Na	Wt% Na by weight of MgO	MgO impregnated with Na(g)	Mo-Fe mixed oxide (g)
2e	2	0.2	0.3	14.7
2f	3	0.2	0.45	14.55
2g	4	0.2	0.6	14.4
2h	5	0.2	0.75	14.25

Table 2

Manual mixing of catalyst components

Calcined MgO: commercial MgO (Sigma-Aldrich, 325 mesh) was calcined, using a static oven with a ramp of 5°C/min, to 1000°C, and kept at target temperature for 2 hours.

- Na impregnated MgO: A batch of the calcined MgO, prepared as described above was prepared and impregnated with NaCl to obtain 0.2wt% Na on the MgO. For that, NaCl was dissolved in enough denim water to fill the pores of the MgO without overfilling for an even distribution of NaCl. The amount of solution required per gram of calcined MgO was 0.60 g/ml. In a glass beaker, 9.98 g of calcined MgO was weighted. In a separate beaker, 0.05 g of NaCl was weighted and dissolved in 6 ml of water. The NaCl solution was added drop wise to the calcined MgO and stirred to ensure good distribution. Then the resulting mixture was dried in an oven at 105°C for ca. 16 hours.

Mo-Fe catalyst: A batch was sieved to a particle size in the range of 250-355 µm.

2i - 1wt% MgO manual mix:

The Mo-Fe catalyst (14.85g) was weighted in a glass beaker and the calcined MgO was added (0.15 g). The reaction mixture was then carefully stirred with a metal spatula during ca. 5 minutes.

- The sample was subsequently calcined at 400 to 550°C to obtain the final catalyst composition.

2j - 1wt% MgO with Na manual mix

The Mo-Fe catalyst (14.85g) was weighted in a glass beaker and the calcined Na impregnated MgO was added (0.15 g). The reaction mixture was then carefully stirred with a metal spatula during ca. 5 minutes.

The sample was subsequently calcined at 400 to 550°C obtain the final catalyst composition.

- Methyl formate selectivity % vs. methanol conversion % was evaluated for 2a-j, along with reference C1.

- The evaluation was carried out in a micro-reactor at 330°C, 0.5 barg and total gas flow 400 Nml/min; the oxygen, methanol, methyl formate, dimethyl ether, formaldehyde, water, and nitrogen concentrations were 7.0, 1.4, 0.2, 0.26, 4.06, 10.0, and 77.08 vol-%, respectively. The weight of the C1 catalyst used in the micro-reactor was 0.1, 0.15, 0.2 and 0.25 g in separate experiments, which gave the respectively increasing levels of conversion shown in Fig. 2. The weight of the catalysts 2a-j used in the micro-reactor test was 0.2 g. Fig. 2 shows that, for 0.2 g catalyst, the methyl formate selectivity was reduced whilst methanol conversion did not drop significantly. It can be extrapolated that this effect would also be seen at higher catalyst loading and methanol conversion. It can also be seen that the preparation of the catalyst is versatile because both RAM and manual mixing provide catalyst showing similar reductions in methyl formate selectivity. The catalyst containing Na shows reduced catalyst activity, but it can be seen by extrapolation that the methyl formate selectivity is even more reduced at a particular methanol conversion.

Example 3

Catalyst compositions were prepared in accordance with the procedures set out in Example 2. However, the Mo-Fe catalyst was calcined at 400 to 550 °C prior to blending or mixing with the MgO or Na impregnated MgO and the final catalyst was not calcined. Catalyst materials having the following compositions were produced.

	wt% MgO	wt% MgO impregnated with Na(g)	Wt% Na by weight of MgO	Blending method
3a	1	-	-	RAM
3b	2	-	-	RAM
3c	3	-	-	RAM
3d	4	-	-	RAM
3e	5	-	-	RAM
3f	-	1	0.2	RAM
3g	-	2	0.2	RAM
3h	-	3	0.2	RAM
3i	-	4	0.2	RAM
3j	-	5	0.2	RAM
3k	1	-	-	Manual
3l	-	1	0.2	Manual

Methyl formate selectivity % vs. methanol conversion % was evaluated for 3a-l, along with reference C1.

The evaluation was carried out in a micro-reactor at 330°C, 0.5 barg and total gas flow 400 Nml/min; the oxygen, methanol, methyl formate, dimethyl ether, formaldehyde, water, and nitrogen concentrations were 7.0, 1.4, 0.2, 0.26, 4.06, 10.0, and 77.08 vol-%, respectively. The weight of the C1 catalyst used in the micro-reactor was 0.1, 0.15, 0.2 and 0.25 g in separate experiments, which gave the respectively increasing levels of conversion shown in Fig. 3. The weight of the catalysts 3a-l used in the micro-reactor test was 0.2 g. Fig. 3 shows that, for 0.2 g catalyst, the methyl formate selectivity was reduced whilst methanol conversion did not drop significantly. It can be extrapolated that this effect would also be seen at higher catalyst loading and methanol conversion. It can also be seen that the preparation of the catalyst composition is versatile because both RAM and manual mixing provide catalyst showing similar reductions in methyl formate selectivity. Again, the catalysts containing Na show reduced catalyst

activity, but it can be seen by extrapolation that the methyl formate selectivity is even more reduced at a particular methanol conversion.

Example 4

4a – 3 wt% ZrO₂ catalyst

- 5 Commercially available ZrO₂ (Alpha Aesar) was sieved to a particle size below 53µm. Then it was calcined, using a static oven with a ramp of 5°C/min, to 1000°C, and kept at target temperature for 2 hours.

An amorphous Mo-Fe catalyst was sieved to a particle size in the range of 250-355 µm.

- 10 The amorphous Mo-Fe catalyst (14.7 g) was added to a reaction pot and the calcined ZrO₂ (0.3 g) was added. The reaction pot was then subjected to RAM using a LabRAM II instrument for 5 minutes at a force of 80g. The sample was subsequently calcined to obtain the final catalyst composition.

4b – 3 wt% ZrO₂:CeO₂ (50:50) catalyst

- 15 A commercially available mixture of CeO₂:ZrO₂ 50:50 (Rhodia) was sieved to a particle size below 53µm. Then it was calcined, using a static oven with a ramp of 5°C/min, to 1000°C, and kept at target temperature for 2 hours.

An amorphous Mo-Fe catalyst sieved to a particle size in the range of 250-355 µm.

The amorphous Mo-Fe catalyst (14.7 g) was added to a reaction pot and the calcined CeO₂:ZrO₂ 50:50 (0.3 g) was added. The reaction pot was then subjected to RAM using a LabRAM II instrument for 5 minutes at a force of 80g. The sample was subsequently calcined to obtain the final catalyst.

- 20 Methyl formate selectivity % vs. methanol conversion % was evaluated for 4a and b, along with reference C1.

- 25 The evaluation was carried out in a micro-reactor at 330°C, 0.5 barg and total gas flow 400 Nml/min; the oxygen, methanol, methyl formate, dimethyl ether, formaldehyde, water, and nitrogen concentrations were 7.0, 1.4, 0.2, 0.26, 4.06, 10.0, and 77.08 vol-%, respectively. The weight of the C1 catalyst used in the micro-reactor was 0.1, 0.15, 0.2 and 0.25 g in separate experiments, which gave the respectively increasing levels of conversion shown in Fig. 4. The weight of the catalysts 4a and b used in the micro-reactor test was 0.2 g. Fig. 4 shows that, for 0.2 g catalyst, the methyl formate selectivity was reduced whilst methanol conversion increased. It can be extrapolated that this effect would also be seen at higher catalyst loading and methanol conversion.

- 30 Example 5

A catalyst was prepared containing 3 wt% MgO following the same methodology described in example 1. Prior to calcination, the catalyst composition was tabletted to give a ring-shaped catalyst table 5a. For tableting, a compaction simulator was used to make single layer pellets and the die fill was carried out by

a vibration feeder. After calcination, the tablet had an outside diameter of 5.1 mm and an inside diameter of 2.75 mm. A conventional lubricant and pore former was used. Reference catalyst C1 was also tableted and calcined, giving a tablet having an outside diameter of 5.0 mm and an inside diameter of 2.75 mm.. The average mass and volume of 10 tablets of each were used to calculate the density of the calcined tablets at room temperature and ambient pressure. A microscope (Infinity 2 model) was used to measure the thickness of the tablet walls. The tablets' hardness in the axial direction, outside diameter, and height were tested using a Sotax hardness tester MT50-FT, Standard, TDH, 800N, 100-240V/50-60Hz. As can be seen in Fig. 5, the tablet containing catalyst composition according to the invention is less dense, which is beneficial for activity of the catalyst, but has a higher hardness. The ability to obtain such a hardness to density ratio means that, for example, tablets with a particular hardness, which may correspond with the hardness of a conventional catalyst pellet, can be prepared at lower densities. This is of great benefit for the durability and stability of the catalyst pellet.

Example 6

Fig. 6 is a TEM image (shown in colour and greyscale) of a coated granule in a catalyst composition of the invention comprising 1 wt% MgO, prepared by the method described above for sample 1b. It can be seen from the image that there is a homogeneous coating of Mg over the surface of the granule of Fe-Mo catalyst material. The surface coating is evident by the higher density of Mg at the edges of the granules in the image in combination with the fact that the blending method used to prepare the catalyst would not lead to impregnation of Mg into the granule.

Fig. 7 is a collection of EDS images (shown in colour and greyscale) of a coated granule in a catalyst composition of the invention comprising 1 wt%, prepared by the method described above for sample 1b. As with Fig. 5, it can be seen from the image that there is a homogeneous coating of Mg over the surface of the granule of Fe-Mo catalyst material. It is also evident that Fe, O and Mo are present throughout the granule.

For TEM and EDS measurements, the samples were ground between two glass slides and dusted onto a holey carbon coated Cu TEM grid. The samples were examined in the JEM 2800 (Scanning) Transmission Electron Microscope using the following instrumental conditions: Voltage (kV) 200; C2 aperture (um) 70 and 40. Dark-field (Z-contrast) imaging in scanning mode using an off-axis annular detector. The SE signal was acquired simultaneously with the other TEM images providing topological information of the sample.

Claims

1. A catalyst composition comprising:
 - i) a catalytic material comprising iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3); and
 - 5 ii) a metal oxide A, wherein the metal oxide A is an alkaline earth metal oxide or zirconium oxide or a combination of zirconium oxide and cerium oxide.
2. The catalyst composition according to claim 1, wherein the metal oxide A is an alkaline earth metal oxide.
3. The catalyst composition according to claim 2, wherein the metal oxide A is magnesium oxide.
- 10 4. The catalyst composition according to claim 1, wherein the metal oxide A is zirconium oxide or a combination of zirconium oxide and cerium oxide.
5. The catalyst composition according to any preceding claim, wherein the catalytic material comprising iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3) is in the form of granules.
6. The catalyst composition according to any preceding claim, comprising a physical blend of the
- 15 catalytic material comprising iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3), and the metal oxide A.
7. The catalyst composition according to claim 5 or claim 6, wherein at least some of the metal oxide A forms a coating around the granules of the catalytic material comprising iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3).
- 20 8. The catalyst composition according to any of claims 5 to 7 comprising:
 - i) granules of the catalytic material comprising iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3); and
 - ii) the metal oxide A;wherein the catalyst composition comprises a physical blend of the catalytic material comprising
- 25 iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3) and the metal oxide A; and
- wherein at least some of the metal oxide A forms a coating around the granules of the catalytic material comprising iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3).
9. The catalyst composition according to any preceding claim, wherein the metal oxide A is present in an amount of no more than about 15 wt% by total weight of the catalyst composition.
- 30 10. The catalyst composition according to any preceding claim, further comprising an alkali metal.

11. The catalyst composition according to any preceding claim, wherein the metal oxide A is impregnated with the alkali metal.
12. The catalyst composition according to claim 10 or claim 11, wherein the alkali metal is present in an amount of no more than about 5 wt% by weight of the metal oxide A.
- 5 13. A pellet comprising the catalyst composition according to any preceding claim.
14. A pellet according to claim 13, having a hardness to density ratio of greater than about 9.
15. A process for the preparation of a catalyst composition according to any of claims 1 to 12, the process comprising the steps of:
- i) calcining a metal oxide A to provide calcined metal oxide A;
- 10 ii) mixing the calcined metal oxide A with a catalytic material comprising iron molybdate ($\text{Fe}_2(\text{MoO}_4)_3$) and molybdenum trioxide (MoO_3);
- iii) calcining the mixture to provide the catalyst composition.
16. The process according to claim 15 for the preparation of a catalyst composition as defined in any of claims 10 to 12, the process comprising a step of:
- 15 ii) impregnating the metal oxide A with the alkali metal using a salt of the alkali metal to provide impregnated metal oxide A prior to calcining the metal oxide A.
17. A process for the production of formaldehyde from methanol comprising the steps of: feeding to a reactor a feed stream comprising the methanol and an oxygen-containing gas; reacting the methanol in the gas phase with the oxygen-containing gas in the reactor in the presence of a catalyst composition
- 20 according to any of claims 1 to 12, or a pellet according to claim 13 or claim 14.
18. A process according to claim 17, wherein the reactor comprises at least one reaction tube, each tube comprising a catalyst bed or beds, wherein the catalyst bed or beds in the lower part of a tube comprises the catalyst composition according to any of claims 1 to 12, or the pellet according to claim 13 or claim 14.
- 25 19. Use of a catalyst composition as defined in any of claims 1 to 13, or a pellet as defined in claim 13 or claim 14, to reduce methyl formate loss in a process for the production of formaldehyde from methanol.
- 30 20. Use according to claim 19, wherein the process comprises the steps of: feeding to a reactor a feed stream comprising the methanol and an oxygen-containing gas; reacting the methanol in the gas phase with the oxygen-containing gas in the reactor in the presence of the catalyst composition; and recovering a formaldehyde reactor outlet stream from the reactor, the formaldehyde reactor outlet stream comprising formaldehyde and methyl formate.