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(54) Title: DIMETHOXYMETHANE PRODUCTION VIA DIRECT HYDROGENATION

(57) Abstract: A process of producing oxymethylene ethers comprising the steps of: a) contacting hydrogen gas and CO and/or CO<sub>2</sub> with a mixture of methanol and a catalyst at conditions of temperature and pressure to support hydrogenation of the CO and/or CO<sub>2</sub> gas in the synthesis gas to oxymethylene ethers; the catalyst comprising: i. catalytic material being at least one metal selected from the group of Ni, Ru, Cu, Pt and Pd; and ii. an acidic catalyst support being at least one selected from the group of zeolites, alumina, amorphous silica-alumina and silica; and b) separating the oxymethylene ethers from the catalyst. Also disclosed herein is a catalyst for the production of dimethoxymethane from synthesis gas in a single contacting step comprising i. catalytic material comprising at least one metal selected from the group of Ni, Pt, Ru, Cu and Pd; and ii. an acidic catalyst support comprising at least one support selected from the group of zeolites, alumina, amorphous silica-alumina and silica.



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## Dimethoxymethane production via direct hydrogenation

### Field of the invention

The present invention relates to the production of dimethoxymethane and in particular to a method of producing dimethoxymethane in a single contact step process.

### 5 Background of the invention

Oxymethylene Ethers (OMEs) are a class of second generation fuel components that can be blended with diesel in large volume fractions to reduce soot emission and to make transportation fuels more sustainable. OMEs can be produced from methanol and formaldehyde using an acid catalyst.

10 The current industrial production method of OME<sub>1</sub> (also known as Dimethoxy Methane, DMM) is based on a two-step process whereby methanol is first partially oxidised into formaldehyde in gas phase in a first reactor, followed by liquid phase acetalization of the as-obtained formaldehyde with methanol in a second reactor. This process suffers from significant losses due to the long chain of reactions starting from  
15 natural gas to produce synthesis gas, followed by methanol synthesis and then partial oxidation of methanol into formaldehyde and then the final step of acetalization to produce OME<sub>1</sub>.

The inventors have recently shown that the formaldehyde synthesis process of the prior art suffers from 57% exergy loss due to this long chain of processes, high  
20 temperature reactions, and large purification steps required. There would be further losses in the production of OME<sub>1</sub> using this route. Recently there has been keen interest in developing alternative methods of OME<sub>1</sub> production, including one-step selective partial oxidation of methanol to OME<sub>1</sub>, however, there are no attempts as yet to produce OME<sub>1</sub> directly from synthesis gas, thereby by-passing the methanol  
25 synthesis completely.

Reference to any prior art in the specification is not an acknowledgment or suggestion that this prior art forms part of the common general knowledge in any jurisdiction or that this prior art could reasonably be expected to be understood,

regarded as relevant, and/or combined with other pieces of prior art by a skilled person in the art.

### Summary of the invention

According to a first aspect of the invention, there is provided a process of  
5 producing dimethoxymethane comprising the steps of:

- a) contacting a synthesis gas of at least CO with a mixture of methanol and a catalyst at conditions of temperature and pressure to support hydrogenation of the CO in the synthesis gas to dimethoxymethane; the catalyst comprising
  - i. catalytic material being at least one metal selected from the group of Ni,  
10 Ru, Cu, Pt and Pd; and
  - ii. an acidic catalyst support being at least one selected from the group of zeolites, alumina, amorphous silica-alumina and silica
- b) separating the dimethoxymethane from the catalyst.

Preferably the catalyst support further includes an acidic ion exchange resin to  
15 increase the acidity of the catalyst support. The synthesis gas which contains at least CO and may also contain CO<sub>2</sub> is fed to a reactor with methanol and catalyst. The catalyst is a bifunctional catalyst which comprises a catalytic metal which catalyses the reaction of synthesis gas and hydrogen to formaldehyde and an acidic catalyst support which catalyses the acetalization of the formaldehyde to dimethoxymethane. The  
20 process of the invention is able to produce dimethoxymethane directly from synthesis gas and methanol in a single contacting step.

The methanol and catalyst is preferably in the form of slurry and the synthesis gas mixed with the slurry in the reactor under conditions which promote hydrogenation. The ratio of CO to hydrogen in the synthesis gas is preferably in the range of 1:1 to 1:20  
25 but is more preferably about 1:2. The conditions to support hydrogenation of the CO in the synthesis gas initially to dimethoxymethane is a temperature in the range of 0 - 200°C, preferably 50 - 150°C, and a pressure of 50-200bar

The catalyst is preferably formed by loading metal oxide catalyst onto an acidic catalyst support which may have been modified to have a size pore structure to which

the metal oxide is loaded. A further catalyst support such as an ion exchange resin may also be added to increase the acidity of the catalyst. The metal oxide on the catalytic support is then reduced to activate the catalytic metal.

5 In a second aspect of the invention, there is provided a process of producing oxymethylene ethers comprising the steps of:

a) contacting a hydrogen gas, CO and/or CO<sub>2</sub> with a mixture of methanol and a catalyst at conditions of temperature and pressure to support hydrogenation of the CO and/or CO<sub>2</sub> gas in the synthesis gas to oxymethylene ethers; the catalyst comprising:

10 i. catalytic material being at least one metal selected from the group of Ni, Ru, Cu, Pt and Pd; and

ii. an acidic catalyst support being at least one selected from the group of zeolites, alumina, amorphous silica-alumina and silica

b) separating the oxymethylene ethers from the catalyst.

15 In an embodiment, the catalyst is a bifunctional catalyst that comprises a catalytic metal which catalyses the reaction of synthesis gas and hydrogen to formaldehyde and an acidic catalyst support which catalyses the acetalization of the formaldehyde to oxymethylene ethers.

20 In an embodiment, the catalyst support further includes an acidic ion exchange resin to increase the acidity of the catalyst support. Preferably, the acidic cation exchange resin is an acidic sulfonic acid cation exchange resin.

In an embodiment, the catalytic material is at least one metal selected from the group of Ni(0), Ru(0), Cu(0), Pt(0) and Pd(0).

In an embodiment, the catalytic material is at least two metals.

25 In an embodiment, the ratio of CO and/or CO<sub>2</sub> to hydrogen in the synthesis gas is from 1:1 to 1:20. Most preferably, the ratio is from about 1:2.

In forms of the invention that include contacting the hydrogen gas with CO, it is preferred that the ratio of CO to hydrogen in the synthesis gas is from 1:1 to 1:20. More preferably, the ratio is from about 1:2.

In forms of the invention that include contacting the hydrogen gas with CO<sub>2</sub>, it is preferred that the ratio of CO<sub>2</sub> to hydrogen in the synthesis gas is from 1:1 to 1:20. More preferably, the ratio is from about 1:2. Most preferably, the ratio is from about 1:3.

In an embodiment, the contacting step is carried out at a temperature of from about 0°C up to about 200°C. Preferably, the temperature is from about 20°C. More preferably, the temperature is from about 40°C. Most preferably, the temperature is from about 50°C. Alternatively, or additionally, it is preferred that the temperature is up to 190°C. More preferably, the temperature is up to 180°C. Most preferably, the temperature is up to 170°C. By way of example, in one form of the invention, the temperature is from 50 up to 150°C.

In an embodiment, the contacting step is carried out at a pressure of from about 50 bar up to about 200 bar. Preferably, the pressure is from about 60 bar. More preferably, the pressure is from about 70 bar. Most preferably, the pressure is from about 75 bar. Alternatively, or additionally, the pressure is up to about 175 bar. More preferably, the pressure is up to about 150 bar. Most preferably, the pressure is up to about 125 bar. By way of example, in one form of the invention, the pressure is from 50 up to 200bar

In an embodiment, the ratio of partial pressure of hydrogen to partial pressure of CO and/or CO<sub>2</sub> is from about 4:1 to about 4:3. Preferably, the ratio of partial pressure of hydrogen to partial pressure of CO and/or CO<sub>2</sub> is about 2:1.

In an embodiment, the oxymethylene ethers comprise, consist, or consist essentially of: OME<sub>1</sub> (dimethoxy methane).

In an embodiment, the oxymethylene ethers comprise, consist, or consist essentially of: OME<sub>1</sub> (dimethoxy methane) and one or more oxymethylene ether oligomers of the form OME<sub>n</sub>, wherein n is an integer of from 2 to 5. It is preferred that n is a 2 or 3, e.g. OME<sub>2</sub> and OME<sub>3</sub>. For avoidance of doubt, OME<sub>n</sub> refers to oxymethylene dimethyl ethers of the form CH<sub>3</sub>(OCH<sub>2</sub>)<sub>n</sub>OCH<sub>3</sub>.

In an embodiment, the contacting step comprises: contacting a synthesis gas including at least: hydrogen gas, CO, and/or CO<sub>2</sub> with the mixture of methanol and the catalyst.

5 In an embodiment, the methanol and catalyst are in the form of slurry and the contacting step comprises mixing the synthesis gas with the slurry in the reactor under conditions which promote hydrogenation.

In an embodiment, the hydrogen gas, CO, and/or CO<sub>2</sub> are introduced to a reactor as synthesis gas and the methanol and catalyst is introduced to the reactor as a slurry.

10 In an embodiment, the process produces oxymethylene ethers from synthesis gas and methanol in a single contacting step.

In a third aspect of the invention, there is provided a catalyst for the production of dimethoxymethane from synthesis gas in a single contacting step comprising: at least one catalytic material selected from the group of Ni, Pt, Ru, Cu and Pd; and at least one acidic catalyst support selected from the group of zeolites, alumina, amorphous silica-  
15 alumina, silica and ion exchange resin.

In an embodiment, the at least one catalytic material is at least one catalytic metal selected from the group of Ni(0), Ru(0), Cu(0), Pt(0) and Pd(0).

20 In an embodiment, the ion exchange resin is an acidic cation exchange resin. Preferably, the acidic cation exchange resin is an acidic sulfonic acid cation exchange resin (e.g. Amberlyst 15 supplied by Dow Chemical).

In an embodiment, at least 2 catalytic metals are used and the support is at least one of the group of zeolites, alumina, amorphous silica-alumina and silica is used in conjunction with the ion exchange resin. The metal/metals may be loaded onto the zeolite, alumina, amorphous silica-alumina or silica and the ion exchange resin is used  
25 to increase the acidity of the catalyst/catalyst support.

Further aspects of the present invention and further embodiments of the aspects described in the preceding paragraphs will become apparent from the following description, given by way of example and with reference to the accompanying drawings.

### Brief description of the drawings

**Figure 1** is a schematic representation of the reaction pathway of synthesis gas to dimethoxymethane;

**Figure 2** is a graph illustrating the yield obtained from the hydrogenation of CO to dimethoxymethane with 0.5 g Ru/Ni on alumina support and 0.5 g acid catalyst/ ion exchange resin (Amberlyst supplied by Dow Chemical).

**Figure 3** is a graph showing the yield obtained from the hydrogenation of CO to dimethoxymethane with a single bifunctional catalyst Ru/Cu on zeolite support.

**Figure 4** is a graph showing the yield obtained from the hydrogenation of CO to dimethoxymethane with a single bifunctional catalyst Ru/Ni on a zeolite support.

**Figure 5** is a schematic diagram of a system to produce dimethoxymethane via a single contacting step process; and

**Figure 6** is a schematic representation illustrating the role of a catalyst or catalysts in the production of dimethoxy methane from hydrogenation of CO.

**Figure 7** is a graph showing the rate of OME<sub>1</sub> production from hydrogenation of CO at various temperatures with (a) Ru-Ni/ $\beta$ -zeolite, (b) Ru-Cu/ $\beta$ -zeolite, (c) B-Ni/ $\beta$ -zeolite, and (d) Ru/ $\beta$ -zeolite.

**Figure 8** is a graph showing the rate of OME<sub>n</sub> production from hydrogenation of CO<sub>2</sub> at temperatures (a) 100 °C (b) 125 °C (c) 150 °C (d) 175 °C.

**Figure 9** is a graph showing the rate of (a) OME<sub>2</sub> (b) OME<sub>3</sub> production from hydrogenation of CO<sub>2</sub> at temperatures (i) 100 °C (ii) 125 °C (iii) 150 °C (iv) 175 °C.

**Figure 10** is a graph showing the rate of OME<sub>1</sub> production from hydrogenation of CO and CO<sub>2</sub> at 150 °C.

### Detailed description of the embodiments

It will be understood that the invention disclosed and defined in this specification extends to all alternative combinations of two or more of the individual features

mentioned or evident from the text or drawings. All of these different combinations constitute various alternative aspects of the invention.

In one form the invention relates to converting CO and/or CO<sub>2</sub> into oxymethylene ethers in a single contacting step via the use of bifunctional nanomaterial catalyst or catalysts with an acidic support. In embodiments thereof, the OMEs include at least dimethoxymethane (OME<sub>1</sub> or DME), as well as dimethoxymethane oligomers including OME<sub>2</sub> and OME<sub>3</sub>. The formation of oligomers of dimethoxymethane, is advantageous as these can be more useful than dimethoxymethane as a diesel substitute. In another form, the invention relates to converting either CO or CO<sub>2</sub> into dimethoxymethane (OME<sub>1</sub> or DMM) in a single contacting step via the use of bifunctional nanomaterial catalyst or catalysts with an acidic support. The invention uses a slurry phase reaction for hydrogenation of CO or CO<sub>2</sub> for the production of OME<sub>1</sub> with the aforementioned catalyst or catalysts. This process, which was carried out in a slurry reactor (**Figure 3**), involves 2 reactions which take place in series (**Figure 1**).

The catalyst or catalysts contain metallic sites (e.g. Ni, Ru, Pt, Cu, Pd, Rh or Re. that are dedicated for CO, CO<sub>2</sub>, and H<sub>2</sub> adsorptions to catalyse the hydrogenation of the CO and CO<sub>2</sub> to formaldehyde and acid sites (e.g. Zeolite, alumina, silicas, amorphous silica-aluminas and ion exchange resin (e.g. Amberlyst 15 available from Dow Chemical)) that further convert intermediate product (formaldehyde) into OME<sub>1</sub>. These bifunctional catalyst or catalysts have high adsorption capacity for CO, CO<sub>2</sub> and H<sub>2</sub>, are stable within methanol as a solvent and contain acid functional sites which promote OME<sub>1</sub> production through dehydration.



Table 1 - Comparison of the specific surface area, total pore volume, amount of active metal, metal dispersion, NiO, Al<sub>2</sub>O<sub>3</sub> and promoter contents of various promoted nickel based catalysts with alumina and zeolite supports.

Catalyst	Nitrogen Physisorption		CO Chemisorption		X-ray Fluorescence Spectroscopy				Support Acidity by NH <sub>4</sub> TPD, mmol g <sup>-1</sup>		
	BET Surface Area (m <sup>2</sup> g <sup>-1</sup> )	BJH Pore Vol. (cc/g) (cm <sup>3</sup> g <sup>-1</sup> )	Irreversible uptake (μmol g <sup>-1</sup> )	Metal Dispersion (%)	NiO (Wt %)	Al <sub>2</sub> O <sub>3</sub> (Wt %)	Theoretical	Measured	Promoter (Wt %)	Weak	Strong
Al <sub>2</sub> O <sub>3</sub>	182	0.18	N.D.	N.D.	-	-	-	-	-	0.103	0.090
Ni-Al <sub>2</sub> O <sub>3</sub>	92	0.21	12.32	0.66	13.59	86.41	86.41	84.09	-	-	-
Pt-Ni-Al <sub>2</sub> O <sub>3</sub>	77	0.14	67.88	3.87	12.37	86.53	86.53	84.30	1.37 <sup>(a)</sup>	-	-
Ru-Ni-Al <sub>2</sub> O <sub>3</sub>	96	0.23	41.96	2.33	12.36	86.44	86.44	86.95	1.03 <sup>(a)</sup>	-	-
Re-Ni-Al <sub>2</sub> O <sub>3</sub>	44	0.07	76.92	4.49	12.36	86.43	86.43	50.42	N.D.	-	-
Rh-Ni-Al <sub>2</sub> O <sub>3</sub>	78	0.15	37.67	2.09	12.36	86.41	86.41	83.72	1.28 <sup>(a)</sup>	-	-
Pt-Ni-Zeolite	524	0.71	N.D.	N.D.	-	-	-	N.D.	0.90	0.502	0.292
Pt-Ni-Zeolite	536	0.63	N.D.	N.D.	-	-	-	N.D.	0.86	0.256	0.215
Pt-Ni-Zeolite (β, 150)	535	0.64	N.D.	N.D.	-	-	-	8.22	1.17	0.142	0.084

<sup>(a)</sup> Calculated based on mass balance

<sup>(b)</sup> Unreacted catalyst

The Zeolite Beta 38, Beta 75 and Beta 150 supports are commercially available catalyst supports but others were made in lab via dealumination procedure to modify the acidity. To increase the Si/Al ratio dealumination was carried out by steam treating the as received zeolite beta followed by removal of dislodged aluminium.

5 Preferably at least 2 catalytic metals are used and the support is at least one of the group of zeolites, alumina, amorphous silica-alumina and silica. The support material may comprise the above support material in conjunction with the ion exchange resin. The metal/metals preferably are loaded onto the zeolite, alumina, amorphous silica-alumina or silica and the ion exchange resin is used to increase the acidity of the  
10 catalyst/catalyst support.

#### Catalyst preparation

Described below is a procedure for the preparation of a Ni/Ru catalyst on an alumina substrate.

Nickel nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) (0 – 10.0 g), alumina ( $\text{Al}_2\text{O}_3$ ) (0 – 20.0 g) and  
15 chemicals such as  $\text{RuCl}_3$  (0 – 0.5 g) were used as the precursors for the catalyst synthesis. First, the required amount of nickel nitrate was measured and dissolved in distilled water. Then, corresponding amount of alumina and metal promoter precursor were added into the solution. To ensure a homogeneous mix of all precursors with alumina, the solution was heated up to 65 °C and maintained for 5hrs under constant  
20 stirring. The solutions were then dried overnight in a 100°C oven. Dry solid were recovered and calcined in a muffle furnace at 600 °C for 6 h under air atmosphere.

To activate the catalyst, the catalyst loaded on the support is reduced by heating it to 400°C under  $\text{H}_2/\text{N}_2$  flow to reduce the metal oxide to pure metal state.

Depending of the metal and catalytic support to be used to make up the  
25 bifunctional catalyst, the person skilled in the art would be able to vary the precursor components and metal activation conditions to produce the required combination of catalytic metals loaded onto the support.

To utilise this process, it is necessary to reduce the metal catalyst first as it is naturally in oxide form and will not react. As a heterogeneous catalyst, these  
30 bifunctional catalyst or catalysts are not consumed in the reaction process. A build-up

of water slows down the reaction and therefore, a process to remove water is required in order to maximise yield. Water can be selectively removed through adsorption with the use of material such as molecular sieve or membrane separation process

As this invention generates OME<sub>1</sub> directly from syngas in a single contacting  
5 step, it removes the long complex process currently utilised and increases the efficiency.

## Examples

### Example 1

The process according to the invention was carried out in accordance with the  
10 process flow diagram illustrated in **Figure 5**. Ex-situ reduced bifunctional catalyst/catalysts was loaded into the reactor along with methanol. These bifunctional catalysts consists of Ni/Ru catalyst with alumina support and acid catalyst- Amberlyst supplied by Dow Chemical. The reactor was first pressurised with high-purity CO and then H<sub>2</sub> based on the required CO:H<sub>2</sub> ratio and its desired pressure (75 bar in this case).

15 The Ni based catalyst was prepared by the impregnation method described earlier and the acid catalyst support was an ion exchange substrate Zeolite or Amberlyst 15). 1.0 g of catalysts (0.5 g Ni/Ru catalyst on alumina support and 0.5 g acid catalyst/ion exchange resin (Amberlyst 15 supplied by Dow Chemical)) was used and the yield of dimethoxymethane at various temperatures (298 – 373 K) under constant  
20 pressure of 75 bar was determined by gas chromatograph. The reaction time was up to around 48 hours. The results are shown in **Figure 2**.

Experiments similar to the above were performed with a Ru/Cu catalyst on a zeolite. The zeolite was Zeolite beta CP814C supplied by Zeolyst International). Synthesis gas having a CO:H<sub>2</sub> ratio of 1:2 was combined with a slurry of a Ru/Cu  
25 catalyst on a zeolite support containing 0.5g of catalyst. **Figure 3** is a graph showing the yield obtained from the hydrogenation of CO to dimethoxymethane with a single bifunctional catalyst Ru/Cu on zeolite support.

Experiments similar to the above were performed with a Ru/Ni catalyst on a zeolite (Zeolite beta CP814C supplied by Zeolyst International). Synthesis gas having a  
30 CO:H<sub>2</sub> ratio of 1:2 was combined with a slurry of a Ru/Cu catalyst on a zeolite support

containing 0.5g of catalyst. **Figure 4** is a graph showing the yield obtained from the hydrogenation of CO to dimethoxymethane with a single bifunctional catalyst Ru/Ni on a zeolite support.

It can be seen from the examples the dimethoxymethane can be produced by a single contacting step process by contact between synthesis gas containing CO and H<sub>2</sub> with a slurry of bifunctional catalyst and methanol.

### Example 2

Catalysts used in this work were synthesized using catalyst preparation method described above.

The catalytic activity of the resultant catalysts was evaluated using a slurry batch high pressure autoclave and the yield of OMEs were quantified using a Shimadzu 2014 GC equipped with ZB-1 capillary column.

Five catalysts were tested in this Example, these catalysts were: Ru-Ni/  $\beta$ -Zeolite, Ru-Cu/  $\beta$ -Zeolite, B-Ni/  $\beta$ -Zeolite, Ru-Ni/ $\gamma$ -alumina and monometallic Ru/  $\beta$ -Zeolite.

**Figure 7** illustrates the rate of OME<sub>1</sub> production from hydrogenation of CO at temperatures of 50 °C, 80 °C, 100 °C, and 120 °C with (a) Ru-Ni/ $\beta$ -zeolite, (b) Ru-Cu/ $\beta$ -zeolite, (c) B-Ni/ $\beta$ -zeolite, and (d) Ru/  $\beta$ -zeolite. The reaction conditions used for (a), (b), and (c) include: H<sub>2</sub>/CO ratio = 2.00, total pressure = 75 bar at room temperature, stirring speed = 100 rpm, catalyst weight = 0.5 g, solvent = methanol (60 ml), runtime =48 hr. (d) Ru/  $\beta$ -zeolite. The reaction conditions for (d) include H<sub>2</sub>/CO<sub>2</sub> ratio = 3.00, total pressure = 75 bar at room temperature, stirring speed = 100 rpm, catalyst weight = 0.5 g, solvent = methanol (50 ml), runtime =360 min. **Figure 7** shows that OME<sub>1</sub> can be produced with these catalysts in methanol as solvent and hydrogen, carbon oxides as reactants.

**Figure 8** compares the rate of production of OME<sub>n</sub> (where n=1, 2, 3) from hydrogenation of CO<sub>2</sub> at (a) 100, (b) 125, (c) 150 and (d) 175 °C with Ru/  $\beta$ -Zeolite. In this case, the reaction conditions were: H<sub>2</sub>/CO<sub>2</sub> ratio = 3.00, total pressure = 75 bar at room temperature, stirring speed = 100 rpm, catalyst = 3% Ru/ $\beta$ -zeolite (0.5g), solvent = methanol (50 ml).

**Figure 8** shows that higher order oligomers of OME<sub>n</sub> (e.g. n= 2, 3) were also produced along with OME<sub>1</sub>, although, in the later stage of the reaction. This suggests that the higher order oligomers were produced via oligomerization of OME<sub>1</sub> with the formaldehyde produced in situ via hydrogenation of CO and CO<sub>2</sub>. Generally, it can be  
5 concluded that production rate of OME<sub>2</sub> and OME<sub>3</sub> increased with an increase of temperature as shown in **Figure 9**.

**Figure 9** reports the rate of production of (a) OME<sub>2</sub> (b) OME<sub>3</sub> via hydrogenation of CO<sub>2</sub> at various temperatures. The reaction conditions used were: H<sub>2</sub>/CO<sub>2</sub> ratio = 3.00, total pressure = 75 bar at room temperature, stirring speed = 100 rpm, catalyst = 3%  
10 Ru/β-zeolite (0.5g), solvent = methanol (50 ml).

A further study was conducted using a different support material (γ-alumina) to investigate the effect of gas reactant (CO and CO<sub>2</sub>) on the yield of OME<sub>1</sub>. The results of this study are summarised in **Figure 10**.

**Figure 10** shows the rate of production of OME<sub>1</sub> from hydrogenation of CO<sub>x</sub> at  
15 150 °C. The reaction conditions used were: H<sub>2</sub>/CO<sub>x</sub> ratio = 2.00, total pressure = 75 bar at room temperature, stirring speed = 100 rpm, catalyst = Ru-Ni/γ-alumina (0.5g), solvent = methanol (60 ml). The results in **Figure 10** indicate that the production rate of OME<sub>1</sub> was at least one fold higher with CO<sub>2</sub> as reactant. This is thought to be as a result of the higher solubility of CO<sub>2</sub> gas in methanol.

20 It will be understood that the invention disclosed and defined in this specification extends to all alternative combinations of two or more of the individual features mentioned or evident from the text or drawings. All of these different combinations constitute various alternative aspects of the invention.

**CLAIMS**

1. A process of producing oxymethylene ethers comprising the steps of:
  - a) contacting hydrogen gas, CO and/or CO<sub>2</sub> with a mixture of methanol and a catalyst at conditions of temperature and pressure to support hydrogenation of  
5 the CO and/or CO<sub>2</sub> gas in the synthesis gas to oxymethylene ethers; the catalyst comprising:
    - i. catalytic material being at least one metal selected from the group of Ni, Ru, Cu, Pt and Pd; and
    - ii. an acidic catalyst support being at least one selected from the  
10 group of zeolites, alumina, amorphous silica-alumina and silica
  - b) separating the oxymethylene ethers from the catalyst.
2. The process of claim 1, wherein the catalytic material is at least one metal selected from the group of Ni(0), Ru(0), Cu(0), Pt(0) and Pd(0).
3. The process of claim 1 or 2, wherein the step of contacting the hydrogen gas  
15 with CO and/or CO<sub>2</sub>, it is preferred that the ratio of CO and/or CO<sub>2</sub> to hydrogen in the synthesis gas is from 1:1 to 1:20.
4. The process of any one of the preceding claims, wherein the contacting step is carried out at a temperature of from about 0°C up to about 200°C.
5. The process of any one of the preceding claims, wherein the contacting step is  
20 carried out at a pressure of from about 50 bar up to about 200 bar.
6. The process of any one of the preceding claims, wherein the ratio of partial pressure of hydrogen to partial pressure of CO and/or CO<sub>2</sub> is from about 4:1 to about 4:3.
7. The process of any one of the preceding claims, wherein the oxymethylene  
25 ethers comprise: OME<sub>1</sub> and one or more oxymethylene ethers oligomers of the form OME<sub>n</sub>, wherein n is an integer of from 2 to 5.
8. The process of claim 7, wherein n is 2 or 3.
9. The process of any one of the preceding claims, wherein the contacting step comprises: contacting a synthesis gas including at least: hydrogen gas, CO, and/or CO<sub>2</sub>  
30 with the mixture of methanol and the catalyst.

10. The process of any one of the preceding claims, wherein the process produces oxymethylene ethers directly from hydrogen gas and CO and/or CO<sub>2</sub> and methanol in a single contacting step.
11. A process of producing dimethoxymethane comprising the steps of:-
- 5 a) contacting a synthesis gas of at least CO with a mixture of methanol and a catalyst at conditions of temperature and pressure to support hydrogenation of the CO in the synthesis gas to dimethoxymethane; the catalyst comprising
- i. catalytic material comprising at least one metal selected from the group of Ni, Pt, Ru, Cu and Pd; and
- 10 ii. an acidic catalyst support comprising at least one support material selected from the group of zeolites, alumina, amorphous silica-alumina and silica;
- b) separating the dimethoxymethane from the catalyst.
12. The process of claim 11 wherein a further catalyst support material comprising
- 15 an ion exchange resin may be added into the catalyst support.
13. The process of claim 11 wherein the conditions to support hydrogenation of the CO in the synthesis gas to dimethoxymethane is a temperature in the range of 0 - 200°C, preferably 50 - 150°C, and a pressure of 50-200bar.
14. The process of any one of claims 11 to 13, wherein the ratio of CO:H<sub>2</sub> in the
- 20 synthesis gas is in the range of 1:1 to 1:20.
15. The process of claim 14 wherein the ration of CO:H<sub>2</sub> is about 1:2.
16. The process of one of claims 11 to 15, wherein the synthesis gas is introduced to a reactor and the methanol and catalyst is introduced to the reactor as a slurry.
17. The process of claim any one of claims 11 to 16, wherein the process produces
- 25 dimethoxymethane directly from synthesis gas and methanol in a single contacting step.
18. A catalyst for the production of dimethoxymethane from synthesis gas in a single contacting step comprising
- i. catalytic material comprising at least one metal selected from the group of Ni, Pt, Ru, Cu and Pd; and

ii. an acidic catalyst support comprising at least one support selected from the group of zeolites, alumina, amorphous silica-alumina and silica.

19. The catalyst of claim 18, wherein the catalyst support further comprises an ion exchange resin.

5 20. The catalyst of claim 18 or 19, wherein the at least one catalytic material is at least one catalytic metal selected from the group of Ni(0), Ru(0), Cu(0), Pt(0) and Pd(0).



FIGURES

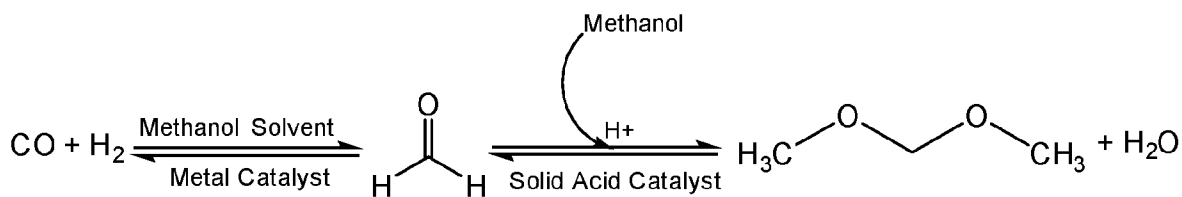


Figure 1

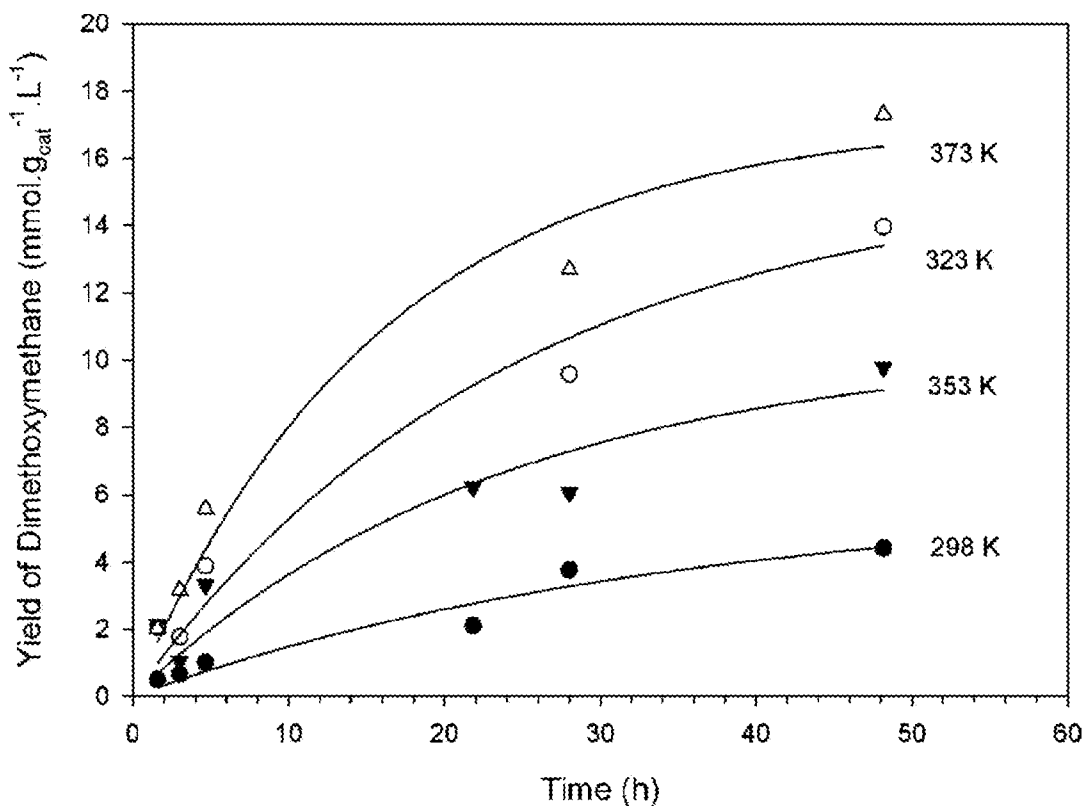


Figure 2

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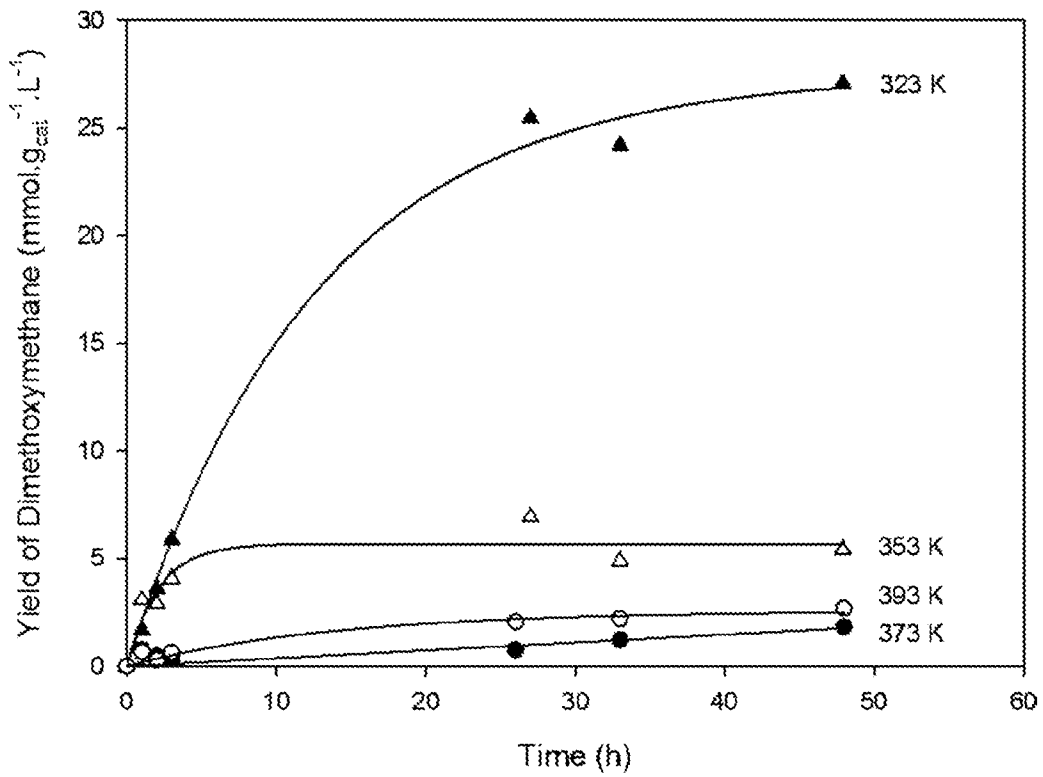


Figure 3

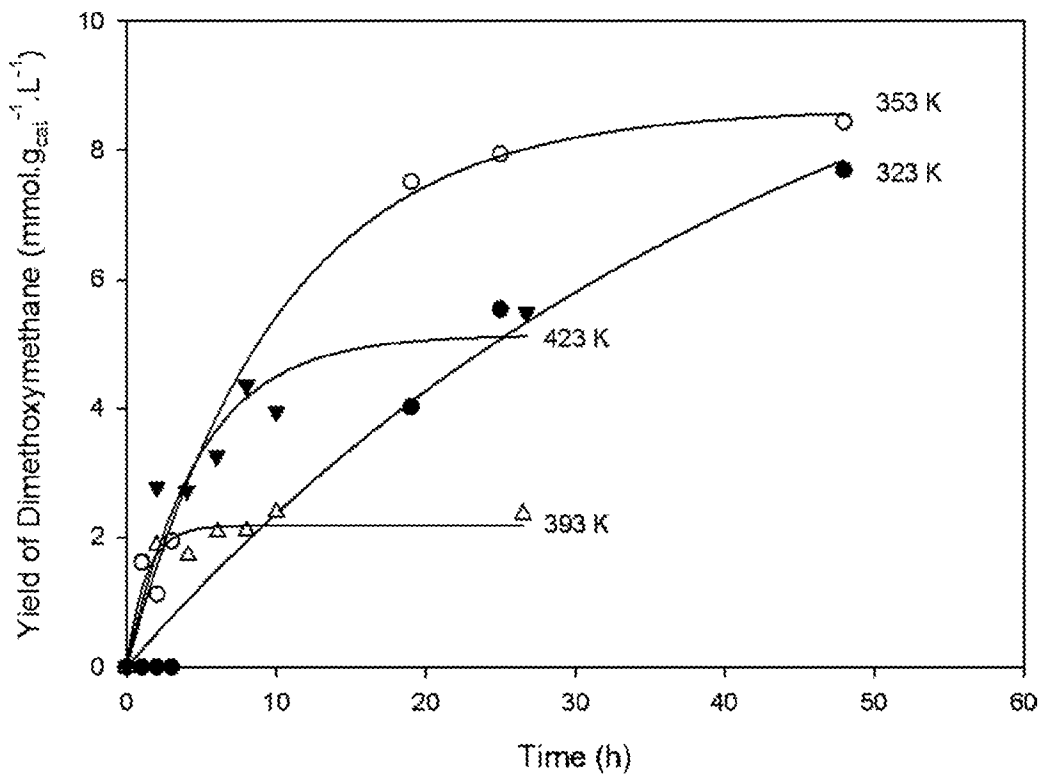


Figure 4

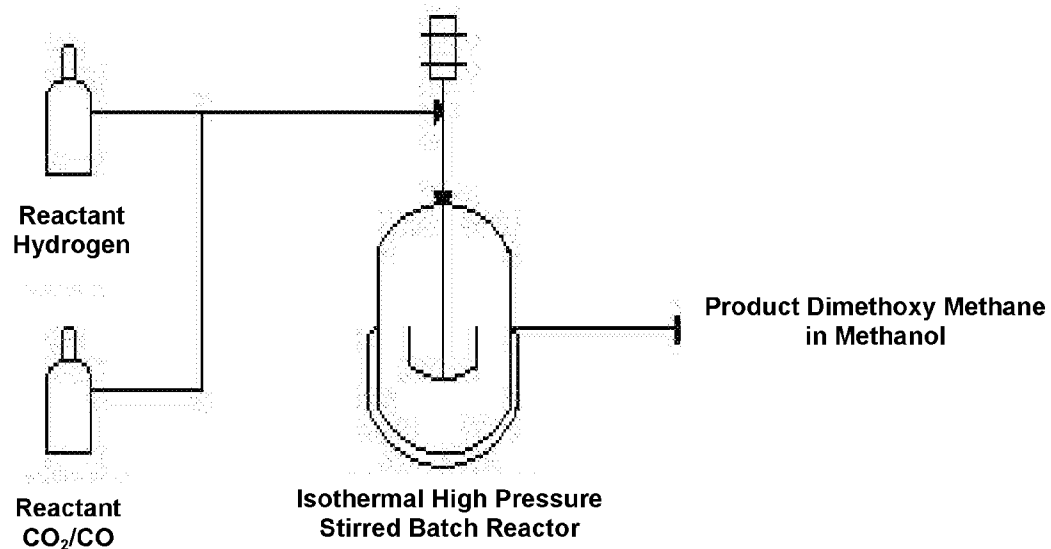


Figure 5

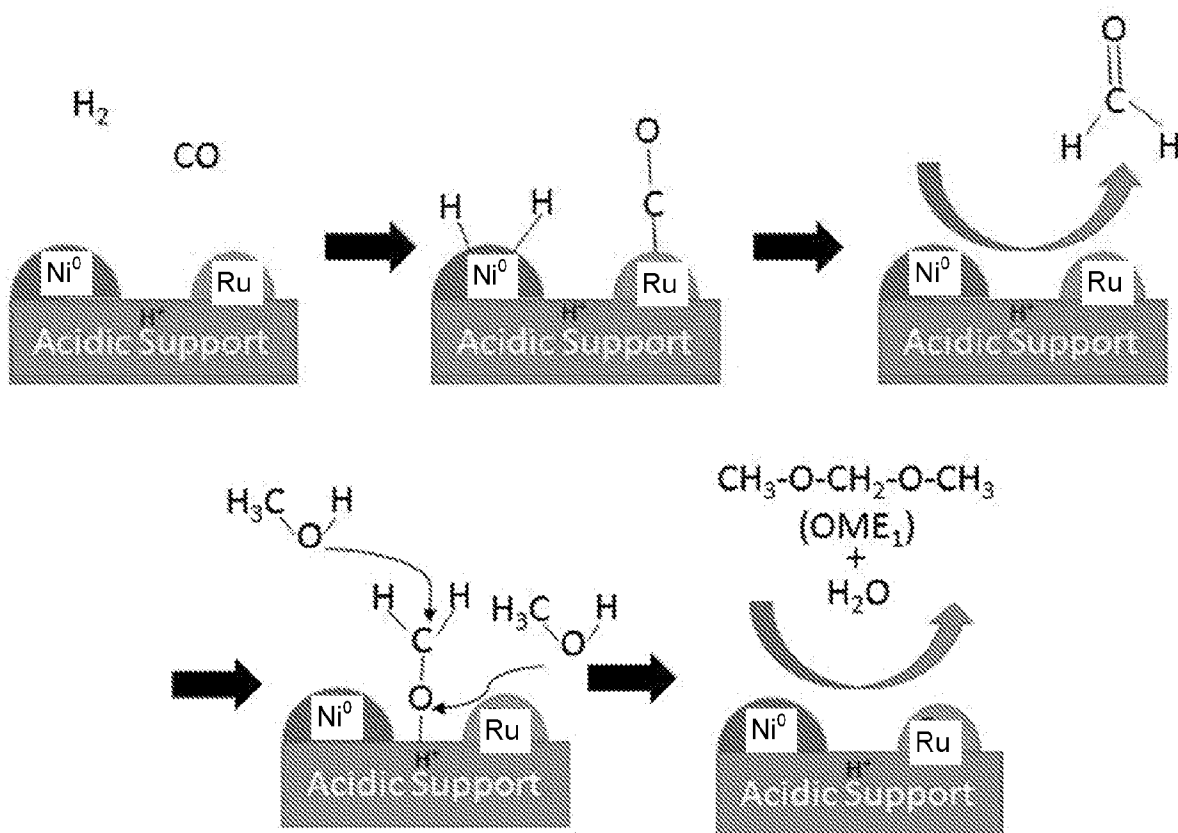


Figure 6

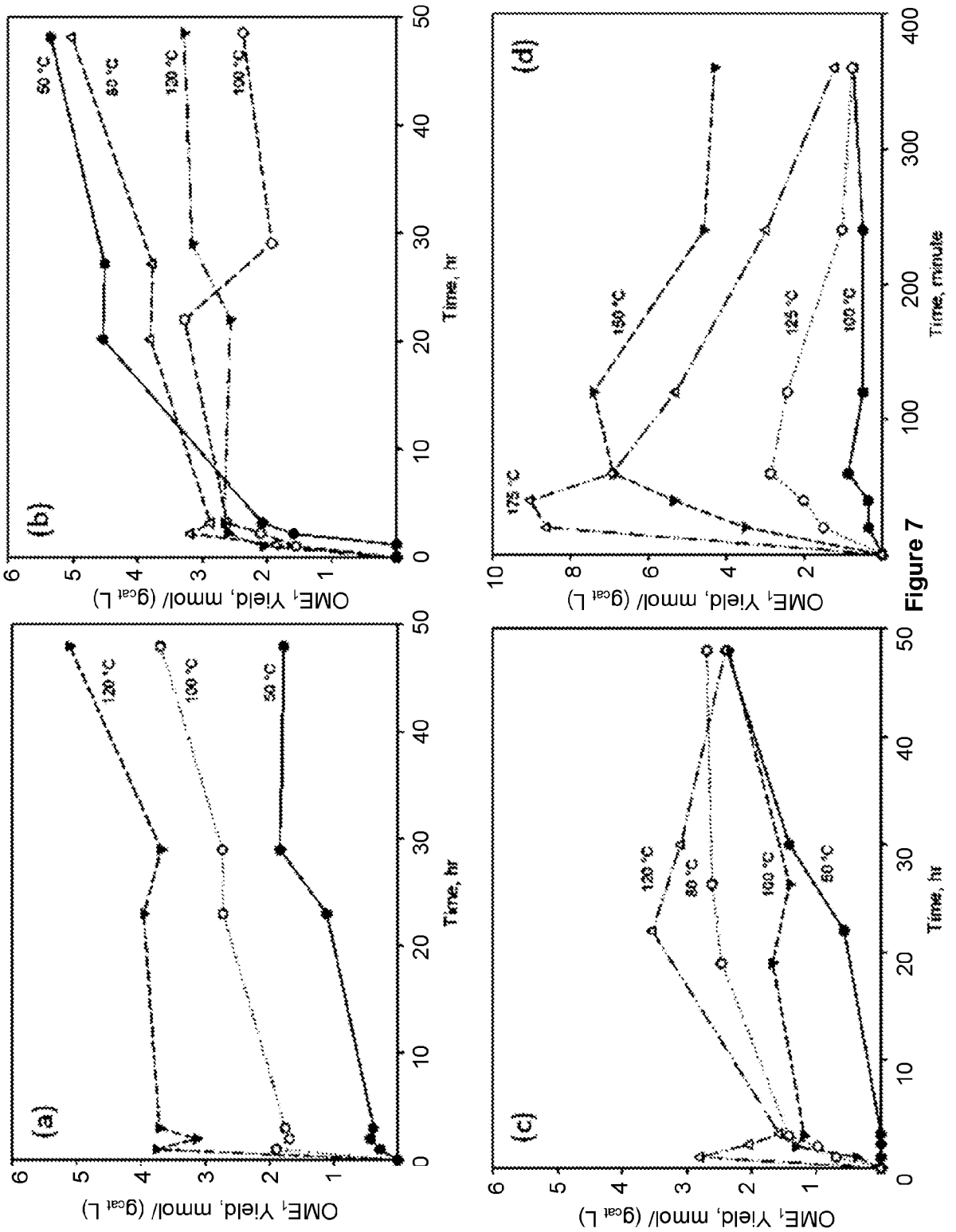


Figure 7

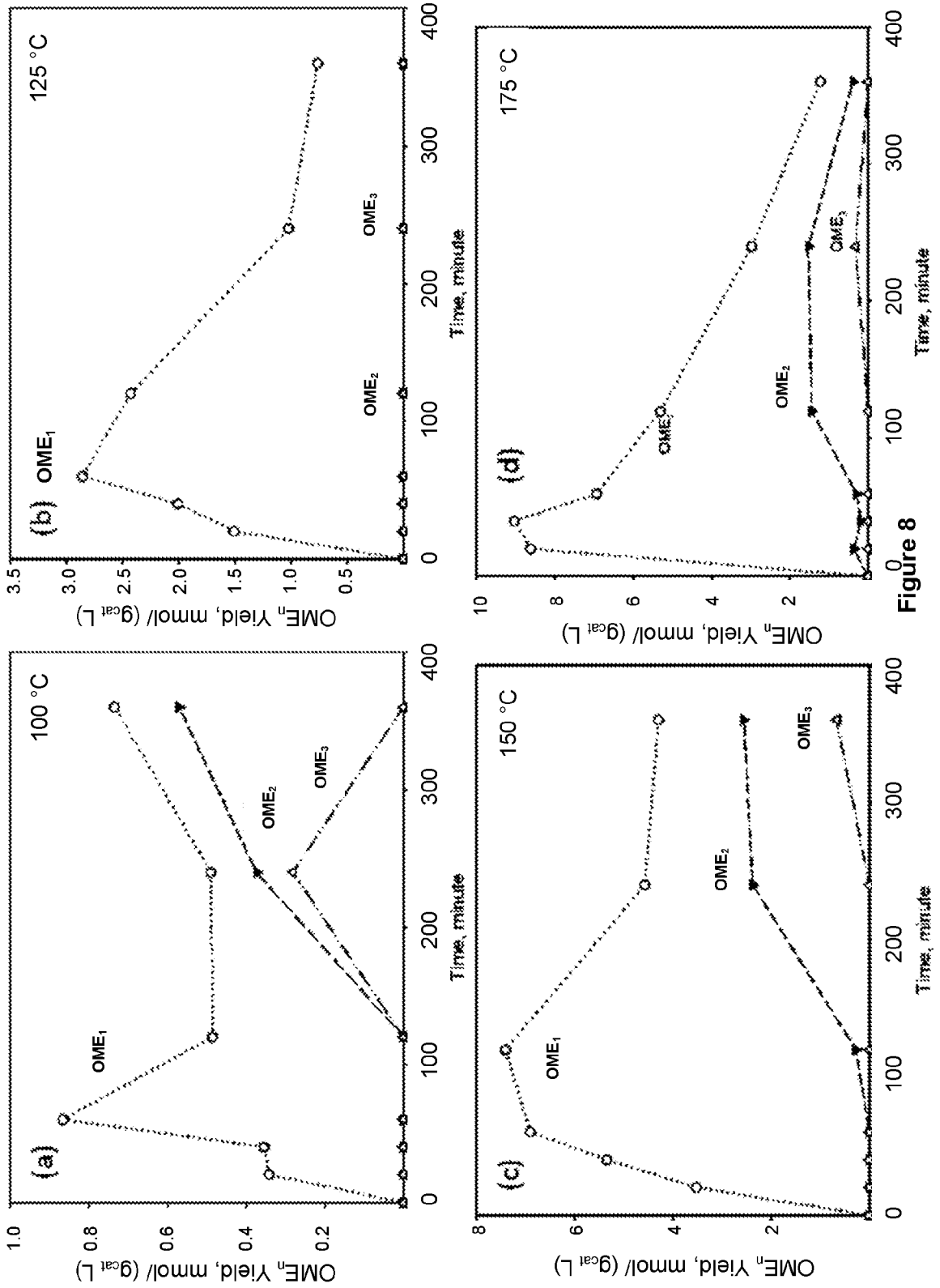


Figure 8

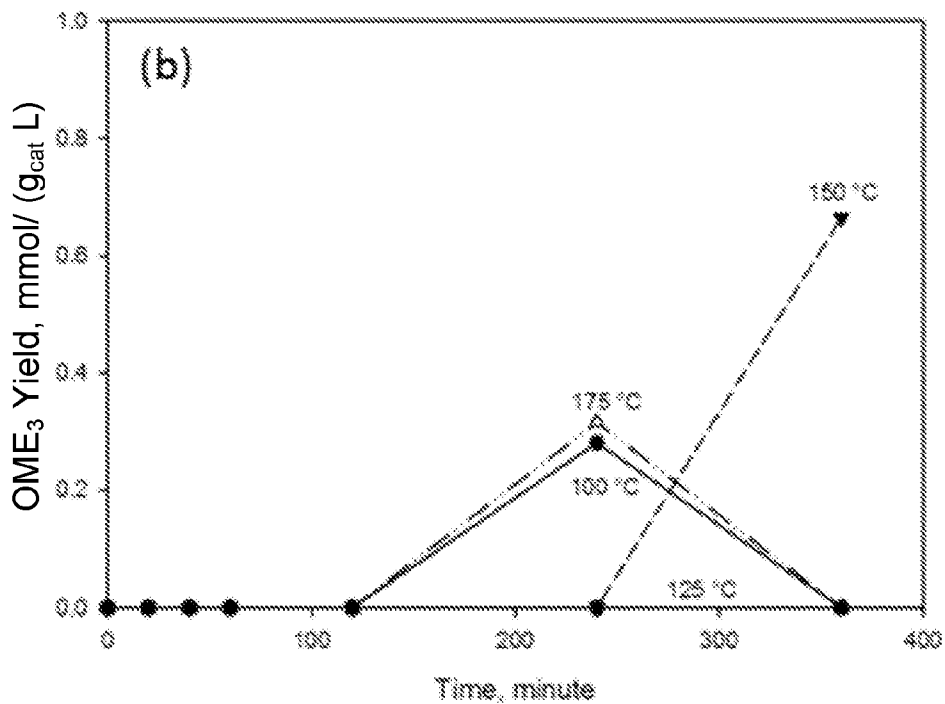
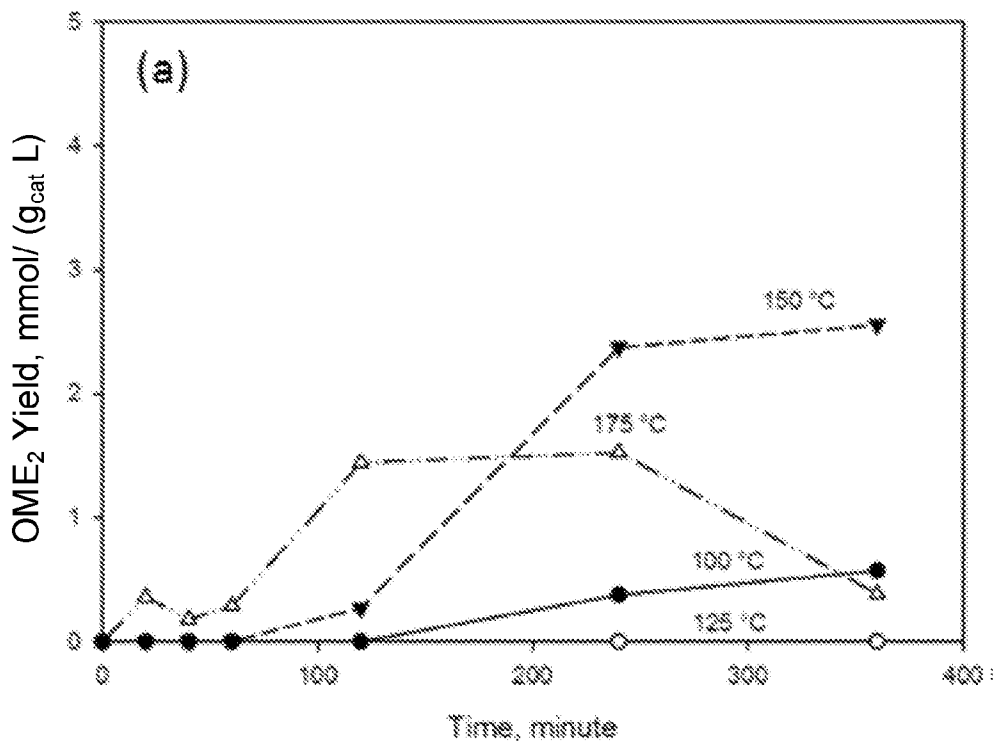


Figure 9

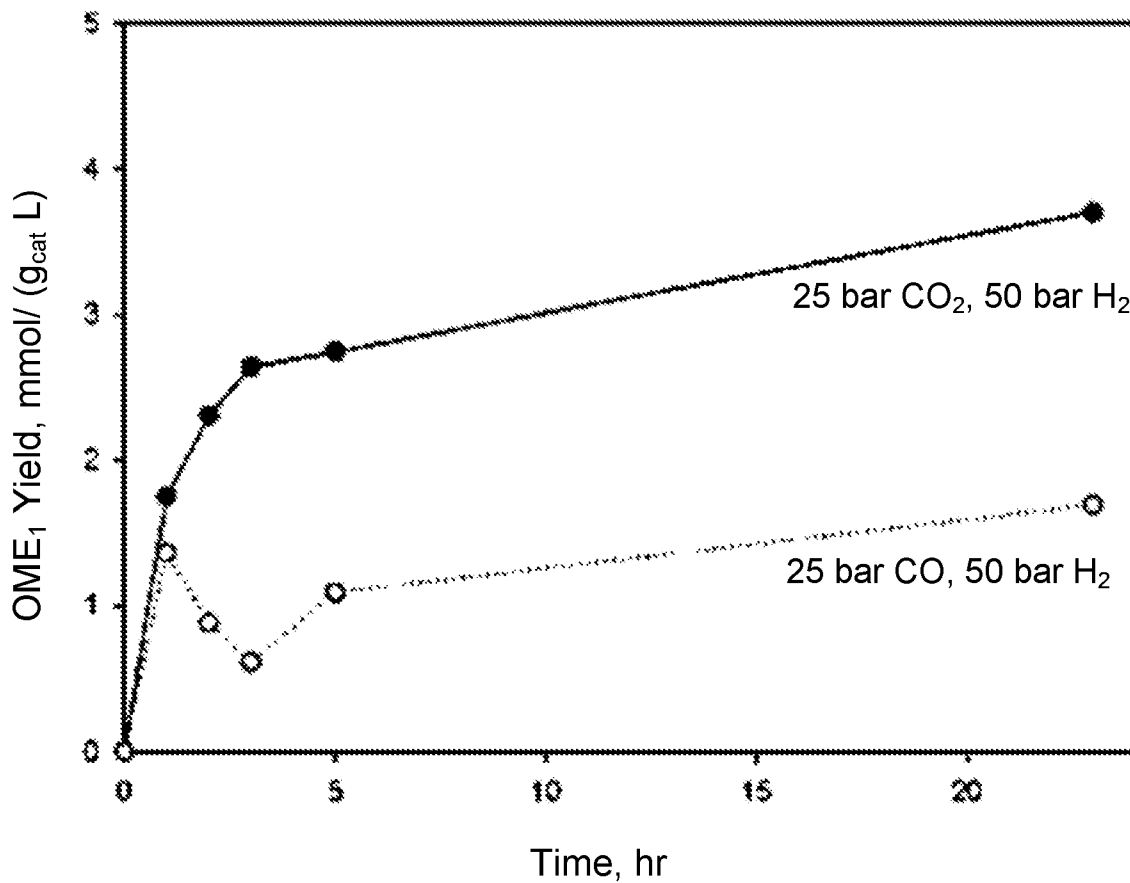


Figure 10



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2018/050746

## A. CLASSIFICATION OF SUBJECT MATTER

**B01J 23/42 (2006.01)**    **B01J 23/44 (2006.01)**    **B01J 23/46 (2006.01)**    **B01J 23/72 (2006.01)**    **B01J 23/755 (2006.01)**  
**B01J 29/06 (2006.01)**    **B01J 29/89 (2006.01)**    **B01J 21/04 (2006.01)**    **B01J 21/12 (2006.01)**    **B01J 21/08 (2006.01)**  
**C07C 41/50 (2006.01)**

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PATENW, CAplus, INSPEC, CNFULL, KRFULL, JPFULL, GOOGLE (PATENTS & SCHOLAR), ESPACENET and IPC/CPC: C07C41/48/LOW, C07C2523/755, C07C2523/42-46, C07C2523/72, C07C2521/04, C07C2521/08, C07C2521/12, B01J2523/17, B01J2523/847, B01J2523/821, B01J2523/824, B01J2523/828, B01J2523/31, B01J2523/41, B01J23/42, B01J23/44, B01J23/462, B01J23/72, B01J23/755), B01J29/06/LOW, B01J29/89, B01J21/04, B01J21/12, B01J21/08 with Keywords: Oxymethylene ether, OME, DMM, dimethoxymethane, syngas, hydrogenation, zeolite, alumina, silica, catalyst, ion-exchange resin, single step and similar terms and/or truncation.

Applicant (MONASH UNIVERSITY) and Inventor (TANKSALE, Akshat OR CHAN, Fan) Names searched in CAplus, INSPEC, ESPACENET, GOOGLE (PATENT & SCHOLAR) and IP Australia internal databases.

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Documents are listed in the continuation of Box C		

 Further documents are listed in the continuation of Box C See patent family annex

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 14 August 2018	Date of mailing of the international search report 14 August 2018
Name and mailing address of the ISA/AU  AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustralia.gov.au	Authorised officer  Luke Sweetman AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. +61262256163

INTERNATIONAL SEARCH REPORT		International application No.
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		<b>PCT/AU2018/050746</b>
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	VLASENKO N. V. et al., 'Direct Single-Stage Conversion of Synthesis Gas to Dimethoxymethane: Influence of the Sequence of Metal Introduction into Cu, Pd-Zeolite Catalysts on the Degree of Cu and Pd Reduction and Catalyst Acidity', Russian Journal of Applied Chemistry, 2013, Vol. 76, Pages 1615-1619. Abstract, Experimental (paragraphs 1-2), Figure 1, Page 1618 (left column)	1-20
X	BAHMANPOUR A., 'Single-step Conversion of Synthesis Gas into Formaldehyde', M. Sc. Thesis, Monash University, 2016. Section 3.2.1	18-20
X	BAHMANPOUR A. M. et al., 'Hydrogenation of Carbon Monoxide into Formaldehyde in Liquid Media', ACS Sustainable Chemistry & Engineering, 2016, Vol. 4, Pages 3970-3977. Experimental	18-20
X	HEIM L. E. et al., 'Future perspectives for formaldehyde: pathways for reductive synthesis and energy storage', Green Chemistry, 16 December 2016, Vol. 19, Pages 2347-2355. Scheme 9	18-20
A	CN 103570485 A (LI JIAN) 12 February 2014	
A	CN 101327444 A (SHANXI COAL CHEM INST) 24 December 2008	

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

**PCT/AU2018/050746**

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

<b>Patent Document/s Cited in Search Report</b>		<b>Patent Family Member/s</b>	
<b>Publication Number</b>	<b>Publication Date</b>	<b>Publication Number</b>	<b>Publication Date</b>
CN 103570485 A	12 February 2014	CN 103570485 A	12 Feb 2014
CN 101327444 A	24 December 2008	CN 101327444 A	24 Dec 2008
		CN 101327444 B	01 Sep 2010

**End of Annex**