ABSTRACT

Carbon dioxide and methane conversion process in methanol using intermetallic compounds or oxide derivatives containing copper and f-block elements as catalysts.

This invention concerns a catalytic process in a heterogeneous phase for converting CO₂ and CH₄ into CH₃OH at low pressure and moderate temperature using binary intermetallics or bimetallic oxides containing copper and f-block elements (lanthanides, U and Th) as catalysts. This invention has an application in the removal and recovery of gaseous pollutants, such as carbon dioxide (CO₂) and methane (CH₄), having been tested and validated under the experimental conditions of catalysts marketed for the synthesis of methanol (CH₃OH). This invention achieves high yields of CH₃OH, thus opening a new path for its synthesis. CH₃OH is an important alternative to fossil fuels, and the technology exists to transform it into other high value chemical products. It can also be used to transport and store hydrogen. By using two gaseous pollutants as reagents, this invention contributes to the reduction of the greenhouse effect.
DESCRIPTION

Carbon dioxide and methane conversion process in methanol using intermetallic compounds or oxide derivatives containing copper and f-block elements as catalysts.

Field of the invention

Technical field in which the invention falls
The present invention describes a catalytic process in a heterogeneous phase for the conversion of carbon dioxide (CO$_2$) and methane (CH$_4$) into methanol (CH$_3$OH) using as catalysts intermetallic binary compounds or bimetallic oxides containing copper (Cu) and f-block elements (Ln = lanthanides and An = actinides, in this case only with U and Th) in their composition, for example CeCu$_2$ and 2CuO.CeO$_2$.
This is the first time that this type of materials has been used for this application. The results obtained are far superior to those that have been described in the literature, in particular when they are compared, under the same conditions, with those of commercial catalysts for the synthesis of methanol.

The use of a primary pollutant such as CO$_2$ for the activation of methane, in opposition to carbon monoxide (CO, a highly toxic gas used by the industry, is also a major benefit with significant environmental impact.

State of the art
Methane, the principal component of natural gas and of biogas, is used in the chemical industry for the production of hydrogen, methanol and synthesis gas (a mixture of hydrogen and carbon monoxide, which can be used to obtain synthetic gasoline through the Fischer-Tropsch process), and other products (M. Behrens, et
The conversion of methane into synthetic gas is based on the "steam reforming" reaction, which consist in the transformation of methane at high temperature in the presence of water vapour (G. Centi, et al, Catalysis for CO₂ conversion: a key technology for rapid introduction of renewable energy in the value chain of chemical industries, Energy Environ. Sci., 2013, 6, 1711-1731). In this process, the catalyst can lose its activity by formation of carbon deposits or by poisoning due to the sulfur present in the natural gas. Currently, methanol is produced industrially starting from mixtures of CO, CO₂ and H₂, a process that occurs at high pressures (>=50 bar) over copper-based catalysts (Cu / ZnO / Al₂O₃) (M. Behrens, et al, The Active Site of Methanol Synthesis over Cu/ZnO/Al₂O₃ Industrial Catalysts, Science 2012, 336, 893-897).

The industrial production of methanol uses a pollutant responsible for the greenhouse effect (CO₂), a toxic gas (CO) and hydrogen (H₂). The process requires high temperatures and pressures (250-600 °C and 50-100 bar, respectively), and therefore the development of a heterogeneous catalytic process, involving the reduction of CO₂ at much lower pressures and temperatures and smaller quantities of CO and H₂ (ideally zero), is a sustainable route to produce methanol and, at the same time, it will contribute to decrease of the greenhouse effect. However, the reaction conditions used until now promote the reverse reaction, the “water gas shift reaction” (WGSR) (reaction 1). This favours the formation of CO which results not only in the reduced production of CH₃OH, but also in a negative effect with respect to the use of methanol in fuel cells (the CO poisons the catalysts based on Pt used in these cells)

\[ \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \] (Reaction 1)
Many of the patented processes use copper catalysts (Cu) (GB1435253(A), RU2006132197(A), WO2008010743(A1)). Nevertheless, the catalysts described are completely different from those used in the present invention. Apart from this, the patented processes involve several steps, carbon monoxide (CO, a toxic gas that all the current industrial processes try to avoid), is used instead of CO$_2$, and sometimes comprise high cost separation/purification methods of non-converted gaseous reagents and products. It should be noted that, except for the most recent one (GB1435253(A)), the other patents are very old and are in Russian, which makes them difficult to read and compare the results.

The ideal alternative for the preparation of methanol would be to use a highly polluting gas, such as, for example, methane as reducing agent (P. Tang, et al, Methane activation: the past and future, Energy Environ. Sci., 2014, 7, 2580-2591). Methane could act at the same time as reducing agent of the CO$_2$ and as source of carbon and H$_2$ (reaction 2).

$$\text{CO}_2 + \text{CH}_4 \leftrightarrow 2\text{CH}_3\text{OH} + 4\text{H}_2 \quad \text{(Reaction 2)}$$

A large number of documents can be found in the literature about the production of methanol (a) US 8980961 B2, b) US 4614749 A, c) US 5827901 A, d) US 4243613 A, e) US 4982023 A). Among the most relevant due to their closeness to our process, we highlight the following (separated based on the reaction mixture used):

- Using synthesis gas (CO + 2H$_2$) as the reaction mixture, Sapienza et al (US 4614749 A) claimed a method of methanol production capable of providing 74% conversion of CO and 94% selectivity for methanol production using organometallic catalysts (complexes of the type NaH-RONa-M(OAc)$_2$, where M=Ni, Pd or Co and R is an alkyl group containing from 1 to 6 carbon atoms) and mild synthesis conditions (80 - 120 °C; 4-70 bar). On the other hand, the process developed by Konig et al (US
5827901 A) can achieve 40 to 80% conversion of carbon monoxide into methanol (catalysts based on CuO.ZnO.Al₂O₃). Other patented processes describe the partial oxidation of CH₄ to methanol, but they are limited by the low rate of conversion of methane (from 0.50 to 9.8%) (US 4243613 A, US 4982023 A).

- Using mixtures of carbon dioxide and hydrogen (H₂/CO₂=3), M. Saito and colleagues (M. Saito, et al; Development of copper/zinc oxide-based multicomponent catalysts for methanol synthesis from carbon dioxide and hydrogen; Applied Catalysis A: General, 1996, 138, 311-318.) claimed yields of methanol of the order of 10 mLCH₃OH/m²cat.h (250 °C, 50 bar), using as catalysts ternary oxides composed of CuO, ZnO and a variable third oxide. In this study a maximum yield of 14 mLCH₃OH/m²cat.h was achieved with the catalyst CuO.ZnO.Ga₂O₃. Under similar conditions, S. Natesakhawat and co-workers (S. Natesakhawat, et al; Active sites and structure-activity relationships of copper-based catalysts for carbon dioxide hydrogenation to methanol; ACS Catalysis, 2012, 2, 1667-1676) claimed higher yields, achieving 170 mLCH₃OH/m²cat.h. A. Bansode and co-workers (A. Bansode, et al, Towards full one-pass conversion of carbon dioxide to methanol-derived products; Journal of Catalysis, 2014, 309, 66-70) have reported a conversion rate of CO₂ of 37% and a selectivity of 74% in methanol at much higher pressures, 360 bar. Under lower pressure conditions (20 bar), D. Jingfa (D. Jingfa, et al; A novel process for preparation of a Cu/ZnO/Al₂O₃ ultrafine catalyst for methanol synthesis from CO₂ + H₂: comparison of various preparation methods; Applied Catalysis A: General, 1996, 139, 75-85) and colleagues obtained comparatively lower rates of conversion (16-19%) and selectivity (22-36%).

- Using mixtures of carbon dioxide, methane and hydrogen, the process that stands out is the one developed by George Olah et al (a) US 8980961 B2). This process claims the conversion of methane into methanol through the bi-reforming of
methane/natural gas (reaction mixture of the type \( \text{CH}_4:\text{H}_2\text{O}:\text{CO}_2 \) (3:2:1) and combination of metals and metal oxides \( \text{V, Ti, Ga, Mg, Cu, Mo, Bi, Fe, Mn, Co, Nb, Zr, La or Sn} \) as catalysts, at high temperatures and pressures: 800-1000 °C and 20-30 bar, respectively. The yield/selectivity is not given.

However, methanol production is strongly dependent on the reaction conditions and catalysts used, as the CO formation through the secondary "dry reforming" reaction (reaction 3) is an important factor that has to be taken into account (P. Tang, et al, Methane activation: the past and future, Energy Environ. Sci., 2014, 7, 2580-2591).

\[ \text{CO}_2 + \text{CH}_4 \leftrightarrow 2\text{CO} + 2\text{H}_2 \]  
(Reaction 3)

Accordingly, the development of better catalysts still remains as the essential step for a cheaper and greener production of methanol. It should be noted that no processes have been found in the literature that claim the production of methanol starting from mixtures containing carbon dioxide, methane and hydrogen, using catalysts (oxides and others) of copper and containing elements of the \( f \)-block of the Periodic Table.

**Summary of the invention**

The present invention describes a catalytic process in a heterogeneous phase for the conversion of carbon dioxide (CO\(_2\)) and methane (CH\(_4\)) into methanol (CH\(_3\)OH), working at low pressures and moderate temperatures. The process uses as catalysts binary intermetallic compounds or bimetallic oxides containing copper (Cu) and \( f \)-block elements (Ln = lanthanides and An = U and Th) in their composition, for example CeCu\(_2\) and 2CuO.CeO\(_2\). It is the first time that this type of materials has been used for this end.

The present invention makes possible to obtain high yields of methanol, especially when compared with the best examples described in the literature, under moderate conditions of pressure and temperature, typically 25-80 bar and 250-320 °C.
The present invention can be used to eliminate and/or obtain added value products from gaseous pollutants such as CO₂ and CH₄, having been tested and validated under the same conditions as other catalysts already marketed for the synthesis of methanol. The present invention is a process which makes a strong contribution to decreasing the greenhouse effect. The product of the present invention is also an important alternative to fossil fuels since the technology exists for the use of methanol as a fuel or fuel additive. In addition, it can be also used for the storage and safety transport of hydrogen.

**Detailed description of the invention**

Figure 1 schematically represents the experimental set-up used in this invention, and can be divided into three parts: A) Mixing and flow control of the gaseous reagents; B) Reactor and reaction chamber, and C) Analysis of the reaction products.

(Figure 1)

A) **Mixing and flow control of the gaseous reagents**

Methane (CH₄) carbon dioxide (CO₂), hydrogen (H₂) and a rare gas (He, helium, which acts as carrier gas) are mixed in well-defined proportions (1:1:3, in the case of reaction A; 1:3, in the case of reaction B, see Table 1). The concentration of the rare gas varies typically between 40-90% for a gas hourly space velocity (GHSV) of 20000 mLCO₂/gcat.h, with the mixing being done at the mixing cross (CM) to ensure a good homogenization. The mixture is injected continuously into the reactor, and by varying the composition of the mixture it is possible to optimize the methanol production. For a stable and reproducible operation, precise control of the flow of gases is required, and this is achieved with mass flow controllers (CF).
B) Reactor and reaction chamber

The reactor is a "Plug&flow" type reactor, operating continuously. The reaction chamber includes a safety valve (VS, with a rupture disk at 200 bar), the reactor (R), a particle filter (F) at the reactor outlet, and upstream pressure controller (CP), with a large working range, 1-200 bar. Downstream the reagents and products leaving the reactor at atmospheric pressure. In region B, comprising the reactor and reaction chamber, all tubing is heated at a temperature between 80 and 100 °C to avoid condensation of liquid products under NTP conditions, namely, condensation of methanol which could produce erroneous results. The stable and reproducible functioning of the reactor requires a precise control of its temperature and pressure (CP).

However, the process main variable is the catalyst. In this process, in contrast to similar ones found in the literature, the catalysts used are intermetallic compounds containing selected f-block elements of (LnCu2, with Ln=lanthanide series and AnCu2, with An=Th, U) and copper. This type of material differs from alloys by having a well-defined crystalline structure and a reproducible preparation. As an alternative, but with fewer advantages, bimetallic oxides containing f-block elements and copper can also be used, for example 3CuO.La2CuO4 or 2CuO.ThO2. The intermetallic compounds are obtained by melting stochiometric quantities of the metals at 900 °C (arc furnace or induction furnace and heating rate of 10 °C/min, while the bimetallic oxides are obtained in a subsequent step by controlled oxidation of the bimetallic compounds at 900 °C (O2/N2 mixture (20:80% by volume) and heating rate of 10 °C/min).

A typical operation involves the following steps (sequential):

1. catalyst weighing, followed by its insertion in the reactor;
2. for a given gas hourly space velocity (GHSV, mL/gcat.h), calculation of the reagents flow rates to be used;
3. reactor on the reaction chamber and introduction of the gaseous reagents, reagents flow on;
4. heating it to the working temperature;
5. reaching such temperature, increase of the pressure up to that required for the process;
6. start of reaction and data collection.

C) Analysis of the reaction products
The products and reactants are analysed continuously, without interfering with the reaction process. For this a 6 port pneumatic valve sampling system (for example, from Supelco), integrated into a chromatographic analysis system (for example, from Agilent) is used. The chromatographic system contains an online detection and analysis system (AOL) allowing the simultaneous analysis of the gases (thermal conductivity detector, TCD) and the analysis of the condensable products, for example methanol (flame ionization detector, FID). With this system it is possible to follow online the conversion of the reagents and formation of all products.

The advantages of this method over those currently used are as follows:
1. High yields and selectivity of methanol formation
The present invention results in higher yields of methanol than the best ones described in the literature (See Table 1).

Table 1. Production of methanol at 250 °C, 50 bar and GHSV=40000 mL/g.h: Reaction A; CH4+CO2+H2 (1:1:3); Reaction B, CO2+H2 (1:3).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction A</th>
<th>Reaction B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Yield CH3OH (mL/m².g)</td>
<td>Selectivity* CH3OH (%)</td>
</tr>
<tr>
<td>LaCu2</td>
<td>3461</td>
<td>88</td>
</tr>
<tr>
<td>CeCu2</td>
<td>1282</td>
<td>86</td>
</tr>
<tr>
<td>Compound</td>
<td>T (°C)</td>
<td>a (%)</td>
</tr>
<tr>
<td>---------------</td>
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</tr>
<tr>
<td>PrCu₂</td>
<td>3740</td>
<td>88</td>
</tr>
<tr>
<td>GdCu₂</td>
<td>2120</td>
<td>88</td>
</tr>
<tr>
<td>TmCu₂</td>
<td>1520</td>
<td>84</td>
</tr>
<tr>
<td>YbCu₂</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cu comercial</td>
<td>66</td>
<td>94</td>
</tr>
<tr>
<td>2CuO.ZnO.Al₂O₃</td>
<td>207</td>
<td>95</td>
</tr>
<tr>
<td>2CuO.CeO₂.Al₂O₃</td>
<td>22</td>
<td>74</td>
</tr>
<tr>
<td>2CuO.CeO₂</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3CuO.La₂CuO₄</td>
<td>268</td>
<td>74</td>
</tr>
</tbody>
</table>


CuO.ZnO.Al₂O₃ 10%AgO - - 9 51 Y. Zhang, et al, Applied Catalysis A: General, 1997, 158, 105-120

PdO.CuO.ZnO - - 18 15 I. Melián-Cabrera, et al, Journal of
* Apart from methanol, only carbon monoxide (CO) was detected as a "secondary" product of the reactions.

The results show clearly that under the same conditions the intermetallic compounds (LnCu₂, with Ln=La, Ce, Pr, Gd e Tm) and the selected bimetallic oxides of the type 3CuO.La₂CuO₄, 2CuO.CeO₂ and 2CuO.ThO₂ are more active than the commercial catalyst, with emphasis on the intermetallic compounds that show an increase in productivity that is various orders of magnitude higher than the best results reported in the literature. Furthermore, even the supported catalysts containing f-block elements (2Cu-M-Al₂O₃, M= Th and Ce), used in this invention and obtained by the same method described for the commercial catalyst, are more active than the commercial catalyst.
2. Low pressure and temperature of the process
The present method avoids the very high temperatures and pressures that the conventional commercial process requires. The reactor where the methanol is produced is a simple “Plug&flow” type reactor that can operate in a wide range of pressures (1-200 bar) at relatively moderate temperatures (25-450 °C).

3. Economic advantages
The method described works under milder conditions (typically 25-80 bar and 250-320 °C) than the conventional ones (250-600 °C and 50-100 bar); additionally, it achieves higher yields of methanol, providing important economic gains (in terms of lower energy for heating the reactor, lower cost materials associated with the lower pressures required for the process, and higher yields of methanol) for the cost of the process.

4. Environmental impacts
Carbon dioxide and methane are two of the most important gases that contribute to the greenhouse effect, showing Global Warning Potential (GWP) of 1 and 72, respectively. Therefore, the methane GWP is 72 times higher than that of carbon dioxide and the reported method has the advantages of allowing the simultaneous elimination/valorisation of these two major pollutant gases, with very high yields in methanol. In addition, the method can be easily adapted to the conversion of methane at the extraction sites, thus avoiding its combustion or release into the atmosphere. The present invention can be used for the valorisation of CO₂ and CH₄, having been tested and validated under the same conditions as commercial catalysts for the synthesis of CH₃OH.

The present invention allows high yields of methanol, especially when compared with the best examples described in the literature, thus opening a new route to the synthesis of methanol under moderate conditions of pressure and temperature.
Description of the Figures

Figure 1 shows schematically the experimental set-up used in this invention, which can be divided into three parts: A) Mixing and flow control of the gaseous reagents; B) Reactor and reaction chamber, and C) Analysis of all products and reagents. Part A includes the reaction gases (He, helium; CH₄, methane; CO₂, carbon dioxide and H₂, hydrogen), shut-off valves (V1), mass flow controllers (CF) and non-return valves (VA). Part B consists of a mixing cross (CM), to homogenize the gases coming from Part A, shut-off valves (V1), the reactor (R), a safety valve (VS) with rupture disc (200 bar), a furnace for heating the reactor, a filter (F) which retains any solid impurity at the reactor outlet (7 micrometres) and a pressure controller (CP). Part B of the set-up is heated up to 80-100 ºC to prevent condensation of some reaction products, i.e. methanol. Finally, Part C consists of an on-line analysis system (AOL) to identify and quantify chromatographically all reagents and products of the reaction.

Lisbon, 16 November 2016
Figure 1
CLAIMS

1. Process for the conversion of carbon dioxide and methane into methanol, characterized by working in a heterogeneous phase at pressures between 25-80 bar, temperatures between 250-350 °C and using as catalysts:
   a) binary intermetallic compounds containing copper and f-block elements;
   b) bimetallic oxides containing copper and f-block elements.

2. Process in agreement with claim 1, characterized by the intermetallic compounds being obtained by melting of the metals at 900 °C, or by any other route.

3. Process in agreement with claim 1, characterized by the bimetallic oxides being obtained by controlled oxidation of the intermetallic compounds at 900 °C, or by any other route.

4. Process in agreement with claim 1, characterized by using binary intermetallic compounds of the type LnCu₂ (Ln=La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) and ThCu₂.

5. Process in agreement with claim 1, characterized by using selected bimetallic oxides containing f-block elements and copper, 2CuO.Ln₂O₃ or 3CuO.Ln₂CuO₄ and 2CuO.ThO₂.

6. Process in agreement with the previous claims, characterized by the addition of hydrogen and H₂/CO₂ (mol:mol) ratios ≥ 3.
7. Process in agreement with the previous claims, characterized by using pure reagents or ones obtained by burning fossil fuel, industrial installation or any other source.

Lisbon, 16 November 2016