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(54) Title: DIMETHYL ETHER COUPLING TO DIMETHOXYETHANE OVER SILVER NANO CATALYSTS

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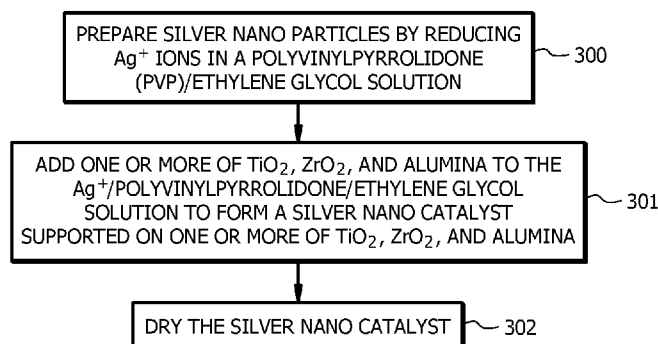


FIG. 3

(57) Abstract: A method of producing dimethoxyethane is disclosed. The method includes contacting molecules of dimethyl ether with a silver nano catalyst under reaction conditions suitable to couple the molecules of dimethyl ether and thereby form the dimethoxyethane. The silver nano catalyst is prepared by reducing Ag⁺ ions in a polyvinylpyrrolidone/ethylene glycol solution.

DIMETHYL ETHER COUPLING TO DIMETHOXYETHANE OVER SILVER NANO CATALYSTS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority of U.S. Provisional Patent
5 Application No. 62/729,149, filed September 10, 2018, which is hereby incorporated by
reference in its entirety.

FIELD OF INVENTION

[0002] The present invention generally relates to the production of dimethoxyethane.
More specifically, the present invention relates to the production of dimethoxyethane by the
10 coupling of dimethyl ether.

BACKGROUND OF THE INVENTION

[0003] 1,2-dimethoxyethane (DMET or dimethoxyethane) is widely used as a solvent.
Dimethoxyethane can be formed by the oxidative coupling of dimethyl ether (DME or
methoxymethane) in the presence of a catalyst. Dimethyl ether, also used as a solvent, is
15 typically produced as a by-product of the organic synthesis of methanol. Conventional
processes for producing dimethoxyethane by the coupling of dimethyl ether has yields of
dimethoxyethane that are very low. Further, in these processes, CO₂ is predominant—the
CO₂ being formed by combustion reactions. Thus, a process of producing dimethoxyethane
that utilizes a catalyst selective for dimethoxyethane and resistant to decomposition is
20 desirable.

BRIEF SUMMARY OF THE INVENTION

[0004] A method has been discovered for producing dimethoxyethane by the coupling
of dimethyl ether under reaction conditions that include contacting the dimethyl ether with a
catalyst that is selective for producing dimethoxyethane and that resists decomposition under
25 the reaction conditions.

[0005] Embodiments of the invention include a method of producing
dimethoxyethane. The method includes contacting molecules of dimethyl ether with a silver

nano catalyst under reaction conditions suitable to couple the molecules of dimethyl ether and thereby form the dimethoxyethane.

[0006] Embodiments of the invention include a method of producing dimethoxyethane that involves preparing a silver nano catalyst. The preparing of the silver nano catalyst includes reducing Ag^+ ions in a polyvinylpyrrolidone (PVP)/ethylene glycol solution and adding one or more of TiO_2 , ZrO_2 , and alumina to the Ag^+ /polyvinylpyrrolidone/ethylene glycol solution to form a silver nano catalyst supported on one or more of TiO_2 , ZrO_2 , and alumina. The method further includes drying the nano catalyst supported on one or more of TiO_2 , ZrO_2 , and alumina. The method further yet includes contacting molecules of dimethyl ether with the silver nano catalyst supported on one or more of TiO_2 , ZrO_2 , and alumina under reaction conditions suitable to couple the molecules of dimethyl ether and thereby form the dimethoxyethane.

[0007] The following includes definitions of various terms and phrases used throughout this specification.

[0008] The terms “about” or “approximately” are defined as being close to as understood by one of ordinary skill in the art. In one non-limiting embodiment the terms are defined to be within 10%, preferably, within 5%, more preferably, within 1%, and most preferably, within 0.5%.

[0009] The terms “wt. %,” “vol. %” or “mol. %” refer to a weight, volume, or molar percentage of a component, respectively, based on the total weight, the total volume, or the total moles of material that includes the component. In a non-limiting example, 10 moles of component in 100 moles of the material is 10 mol.% of component.

[0010] The term “substantially” and its variations are defined to include ranges within 10%, within 5%, within 1%, or within 0.5%.

[0011] The terms “inhibiting” or “reducing” or “preventing” or “avoiding” or any variation of these terms, when used in the claims and/or the specification, include any measurable decrease or complete inhibition to achieve a desired result.

[0012] The term “effective,” as that term is used in the specification and/or claims, means adequate to accomplish a desired, expected, or intended result.

[0013] The use of the words “a” or “an” when used in conjunction with the term “comprising,” “including,” “containing,” or “having” in the claims or the specification may mean “one,” but it is also consistent with the meaning of “one or more,” “at least one,” and “one or more than one.”

5 [0014] The words “comprising” (and any form of comprising, such as “comprise” and “comprises”), “having” (and any form of having, such as “have” and “has”), “including” (and any form of including, such as “includes” and “include”) or “containing” (and any form of containing, such as “contains” and “contain”) are inclusive or open-ended and do not exclude additional, unrecited elements or method steps.

10 [0015] The process of the present invention can “comprise,” “consist essentially of,” or “consist of” particular ingredients, components, compositions, etc., disclosed throughout the specification.

[0016] The term “primarily,” as that term is used in the specification and/or claims, means greater than any of 50 wt. %, 50 mol. %, and 50 vol. %. For example, “primarily”
15 may include 50.1 wt. % to 100 wt. % and all values and ranges there between, 50.1 mol. % to 100 mol. % and all values and ranges there between, or 50.1 vol. % to 100 vol. % and all values and ranges there between.

[0017] Other objects, features and advantages of the present invention will become apparent from the following figures, detailed description, and examples. It should be
20 understood, however, that the figures, detailed description, and examples, while indicating specific embodiments of the invention, are given by way of illustration only and are not meant to be limiting. Additionally, it is contemplated that changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description. In further embodiments, features from specific embodiments may be
25 combined with features from other embodiments. For example, features from one embodiment may be combined with features from any of the other embodiments. In further embodiments, additional features may be added to the specific embodiments described herein.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] For a more complete understanding, reference is now made to the following descriptions taken in conjunction with the accompanying drawings, in which:

[0019] FIG. 1 shows a system for producing dimethoxyethane, according to
5 embodiments of the invention;

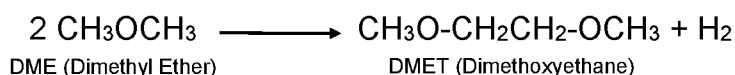
[0020] FIG. 2 shows a method of producing dimethoxyethane, according to
embodiments of the invention; and

[0021] FIG. 3 shows a method of producing a catalyst for coupling dimethyl ether to
produce dimethoxyethane, according to embodiments of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0022] A method has been discovered for producing dimethoxyethane by the coupling
of dimethyl ether under reaction conditions that include contacting the dimethyl ether with a
catalyst that is selective for producing dimethoxyethane and that resists decomposition under
reaction conditions suitable for the coupling. The method makes use of metal nanoparticles
15 as the catalyst in forming dimethoxyethane from the coupling of dimethyl ether.

[0023] In embodiments of the invention, supported metal nano catalysts such as any
of silver (Ag) gold (Au), and platinum (Pt) supported on any of TiO₂, ZrO₂, and Al₂O₃
catalyze dimethyl ether to form coupling products in vapor phase fixed bed reactions. Nano
metal catalysts sites activate oxygen to form oxide radical under the reaction conditions
20 followed by abstraction of methoxy-H and form methoxy methyl radical that further
undergoes rearrangement to form the coupling product *i.e.*, dimethoxyethane. Thus, the
vapor phase oxidative coupling of dimethyl ether can produce dimethoxyethane (reaction
shown below).



[0024] FIG. 1 shows system 10 for producing dimethoxyethane, according to
embodiments of the invention. FIG. 2 shows method 20 for producing dimethoxyethane,

according to embodiments of the invention. Method 20 may be implemented by using system 10.

[0025] Method 20 at block 200, as implemented by system 10, involves providing catalyst 101 in reactor 100, in embodiments of the invention. Reactor 100 may be a fixed bed reactor or a fluidized bed reactor. In embodiments of the invention, reactor 100 is a fixed bed down flow reactor. According to embodiments of the invention, catalyst 101 is adapted so that it is selective for the formation of dimethoxyethane in a coupling reaction of dimethyl ether molecules.

[0026] FIG. 3 shows method 30 for producing catalyst 101 that involves adapting the catalyst so that it is selective for the formation of dimethoxyethane in a coupling reaction of dimethyl ether molecules, according to embodiments of the invention. Catalyst 101, in embodiments of the invention, can include silver (Ag) nano particles supported on one or more of: TiO₂, ZrO₂, and alumina. Synthesis of catalyst 101 can begin at block 300, which involves preparing silver nano particles. Preparing silver nano particles at block 300 may include reducing Ag⁺ ions in a polyvinylpyrrolidone (PVP)/ethylene glycol solution. In embodiments of the invention, the reduction of Ag⁺ ions in a polyvinylpyrrolidone/ethylene glycol solution can be carried out at a temperature in a range of 170 °C to 190 °C, and all values and ranges therebetween, including 170 to 172 °C, 172 to 174 °C, 174 to 176 °C, 176 to 178 °C, 178 to 180 °C, 180 to 182 °C, 182 to 184 °C, 184 to 186 °C, 186 to 188 °C, and 188 to 190 °C, preferably 180 °C. The size of the nano particles can be controlled, at least in part, by varying the polyvinylpyrrolidone/Ag⁺ ratio.

[0027] According to embodiments of the invention, block 301 involves adding one or more of TiO₂, ZrO₂, and alumina to the Ag⁺/polyvinylpyrrolidone/ethylene glycol solution as support to form a silver nano catalyst supported on one or more of TiO₂, ZrO₂, and alumina. The addition of TiO₂, ZrO₂, and alumina to the Ag⁺/polyvinylpyrrolidone/ethylene glycol solution at block 301 may include the use of incipient wetness impregnation to form the silver nano catalyst supported on one or more of TiO₂, ZrO₂, and alumina. TiO₂, ZrO₂, and alumina support material may be purchased from Sigma-Aldrich® or synthesized by sol-gel methods.

[0028] In embodiments of the invention, method 30 further includes block 302, which involves drying the resulting silver nano catalyst supported on one or more of TiO₂, ZrO₂,

and alumina at a temperature in a range of 110 °C to 130 °C for a period of 6 to 24 hours. The average particle size of the silver nano catalyst supported on one or more of TiO₂, ZrO₂, and alumina can be in a range of 1 to 100 nm. This silver nano catalyst supported on one or more of TiO₂, ZrO₂, and alumina is selective for the formation of dimethoxyethane in a coupling reaction of dimethyl ether molecules and may be used as catalyst 101 in
5 embodiments of the invention. Examples of silver nano catalysts, in embodiments of the invention, include 1% Ag nano/ZrO₂ and 1% Ag nano/TiO₂.

[0029] Returning to method 20, once catalyst 101 (*e.g.*, a silver nano catalyst supported on one or more of TiO₂, ZrO₂, and alumina) is provided in reactor 100 at block
10 200, method 20 may continue at block 201 with the flowing of dimethyl ether, of feed 102, into reactor 100. Block 202 of method 20 can therefore involve, in embodiments of the invention, contacting the dimethyl ether with catalyst 101 at conditions suitable for causing dimethyl ether molecules to couple with one another and form dimethoxyethane.

[0030] The conditions suitable for causing dimethyl ether molecules to couple in the
15 presence of catalyst 101 to form dimethoxyethane includes a temperature in a range of 250 °C to 300 °C and all values and ranges therebetween, including 250 to 255 °C, 255 to 260 °C, 260 to 265 °C, 265 to 270 °C, 270 to 275 °C, 275 to 280 °C, 280 to 285 °C, 285 to 290 °C, 290 to 295 °C, 295 to 300 °C.

[0031] The conditions suitable for causing dimethyl ether molecules to couple in the
20 presence of catalyst 101 to form dimethoxyethane includes a pressure in a range of 15 to 25 atm and all values and ranges therebetween, including 15 to 16 atm, 16 to 17 atm, 17 to 18 atm, 18 to 19 atm, 19 to 20 atm, 20 to 21 atm, 21 to 22 atm, 22 to 23 atm, 23 to 24 atm, 24 to 25 atm.

[0032] The conditions suitable for causing dimethyl ether molecules to couple in the
25 presence of catalyst 101 to form dimethoxyethane includes a GHSV in a range of 6000 to 10000, all values and ranges therebetween, and preferably 7895 h⁻¹.

[0033] At block 203, in embodiments of the invention, effluent 103, comprising 5 to 19 wt. % dimethoxyethane, 80 to 94 wt. % dimethyl ether, 1 to 2 wt. % hydrogen (H₂) is flowed from reactor 100. At block 204, dimethoxyethane is recovered from effluent 103 by
30 one or more separation methods including gas-liquid separation or distillation (separation on the basis of boiling point).

[0034] Although embodiments of the present invention have been described with reference to blocks of FIG. 2 and FIG. 3, it should be appreciated that operation of the present invention is not limited to the particular blocks and/or the particular order of the blocks illustrated in FIG. 2 and FIG. 3. Accordingly, embodiments of the invention may provide functionality as described herein using various blocks in a sequence different than that of FIG. 2 and FIG. 3.

EXAMPLES

[0035] As part of the disclosure of the present invention, a specific example is included below. The example is for illustrative purposes only and is not intended to limit the invention. Those of ordinary skill in the art will readily recognize parameters that can be changed or modified to yield essentially the same results.

Example
(Coupling of DME in the presence of silvery nano catalysts)

Catalyst	Temperature (°C)	Pressure	(mol%) DME Conversion	Selectivity to DMET (mol%)
		(bar)		
1%Ag Nano/ZrO ₂	300	25	11.8	3.9
		15	13.9	2.5
1%Ag Nano/TiO ₂	300	25	3.8	9.4
		15	5.7	11.3

Table 1

[0036] Experiments were conducted to determine the rate of conversion of dimethyl ether and selectivity of dimethoxyethane achievable in the coupling of dimethyl ether in the presence of two silver nano catalysts, namely 1% Ag nano/ZrO₂ and 1% Ag nano/TiO₂. In the experiments, dimethyl ether was contacted with % Ag nano/ZrO₂ and 1% Ag nano/TiO₂ catalysts separately under the conditions shown in Table 1. The conversion rate and selectivity of dimethoxyethane that resulted was determined and are also shown in Table 1.

[0037] In the context of the present invention, embodiments 1-15 are described. Embodiment 1 is a method of producing dimethoxyethane. The method includes contacting molecules of dimethyl ether with a silver nano catalyst under reaction conditions suitable to couple the molecules of dimethyl ether and thereby form the dimethoxyethane. Embodiment 2 is the method of embodiment 1, wherein the silver nano catalyst is supported on an oxide of zirconium and/or an oxide of titanium. Embodiment 3 is the method of either of

embodiments 1 or 2, wherein the silver nano catalyst contains one or more of Ag nano/ZrO₂ and 1% Ag nano/TiO₂. Embodiment 4 is the method of embodiment 1, wherein the silver nano catalyst is supported on alumina. Embodiment 5 is the method of any of embodiments 1 to 4, wherein the reaction conditions include a temperature in a range of 250 °C to 300 °C.

5 Embodiment 6 is the method of any of embodiments 1 to 5, wherein the reaction conditions include a pressure of 15 atm to 25 atm. Embodiment 7 is the method of any of embodiments 1 to 6, wherein the reaction conditions include a GHSV of 6000 to 10000 h⁻¹. Embodiment 8 is the method of any of embodiments 1 to 7, wherein the silver nano catalyst includes an average particle size in a range of 1 to 100 nm. Embodiment 9 is the method of any of

10 embodiments 1 to 8, wherein the molecules of dimethyl ether are in vapor phase during the contacting. Embodiment 10 is the method of any of embodiments 1 to 9, wherein the contacting is carried out in a fixed bed flow reactor. Embodiment 11 is the method of any of embodiments 1 to 10, wherein the silver nano catalyst is prepared in a process including reducing Ag⁺ ions in a polyvinylpyrrolidone/ethylene glycol solution to form a

15 Ag⁺/polyvinylpyrrolidone/ethylene glycol solution, and adding one or more of TiO₂, ZrO₂, and alumina to the Ag⁺/polyvinylpyrrolidone/ethylene glycol solution to form the silver nano catalyst, wherein the silver nano catalyst is supported on one or more of TiO₂, ZrO₂, and alumina, then drying the silver nano catalyst. Embodiment 12 is the method of embodiment 11, wherein the reducing of Ag⁺ ions is carried out in the polyvinylpyrrolidone/ethylene

20 glycol solution at a temperature in a range of 170 °C to 190 °C. Embodiment 13 is the method of either of embodiments 11 or 12, wherein the adding of the one or more of TiO₂, ZrO₂, and alumina is carried out by incipient wetness impregnation. Embodiment 14 is the method of any of embodiments 11 to 13, wherein the drying is carried out at a temperature of 110 °C to 130 °C. Embodiment 15 is the method of any of embodiments 11 to 13, wherein

25 the drying is carried out in a period of 6 to 24 hours.

[0038] Although embodiments of the present application and their advantages have been described in detail, it should be understood that various changes, substitutions and alterations can be made herein without departing from the spirit and scope of the embodiments as defined by the appended claims. Moreover, the scope of the present

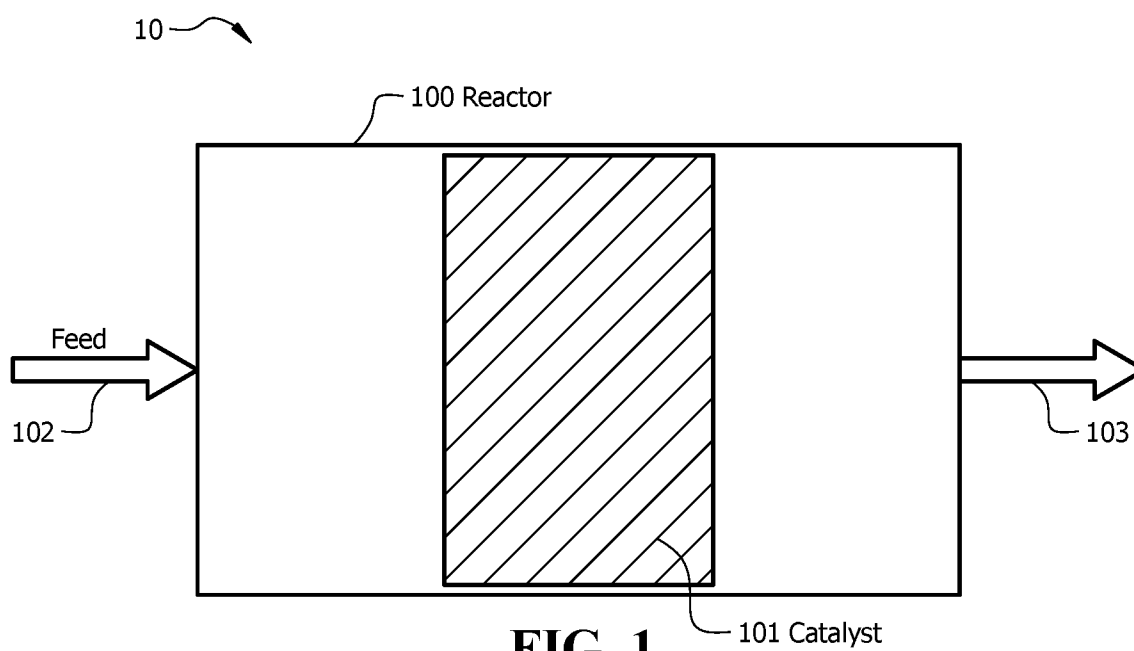
30 application is not intended to be limited to the particular embodiments of the process, machine, manufacture, composition of matter, means, methods and steps described in the specification. As one of ordinary skill in the art will readily appreciate from the above disclosure, processes, machines, manufacture, compositions of matter, means, methods, or

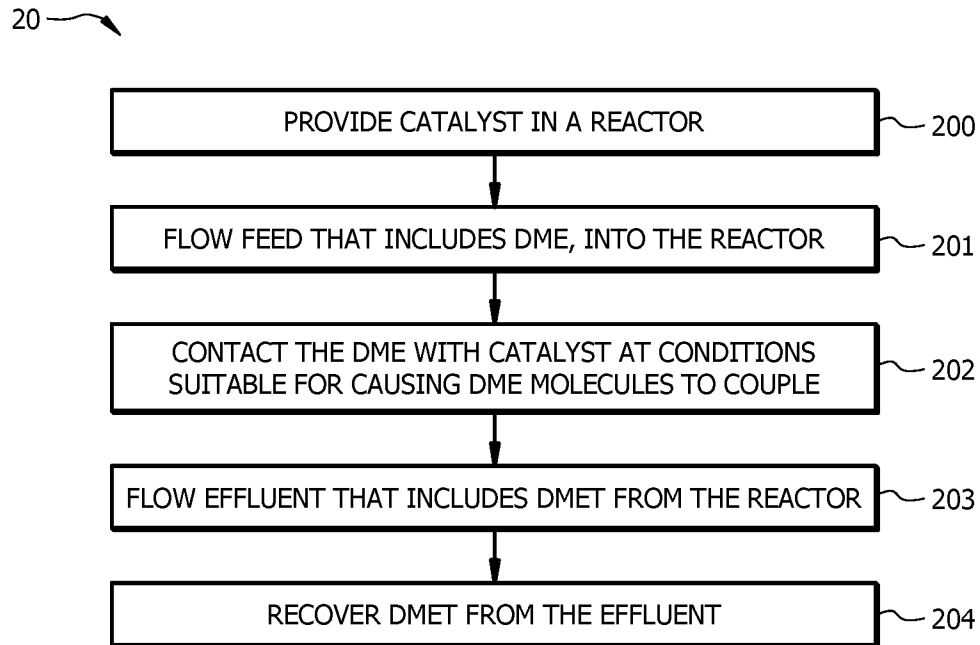
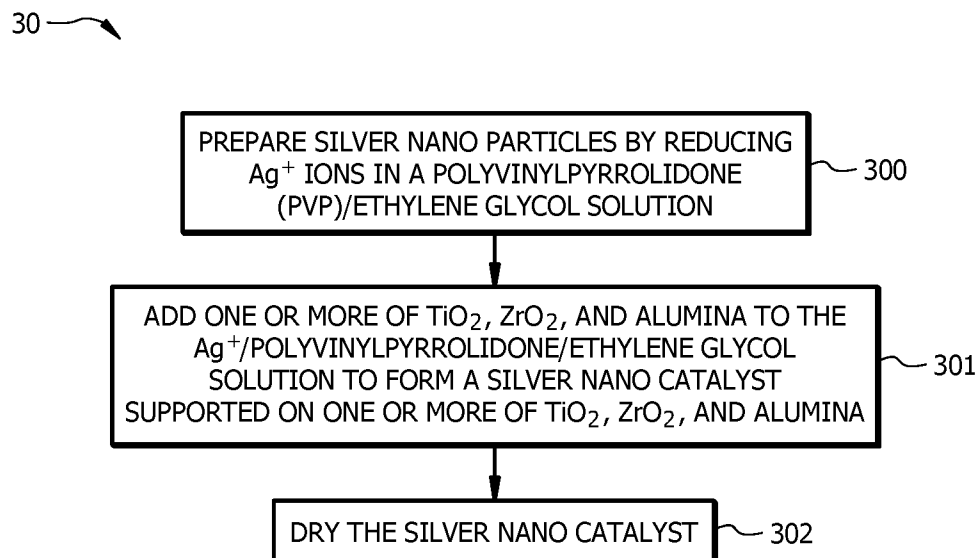
steps, presently existing or later to be developed that perform substantially the same function or achieve substantially the same result as the corresponding embodiments described herein may be utilized. Accordingly, the appended claims are intended to include within their scope such processes, machines, manufacture, compositions of matter, means, methods, or steps.

CLAIMS

1. A method of producing dimethoxyethane, the method comprising:
contacting molecules of dimethyl ether with a silver nano catalyst under reaction conditions suitable to couple the molecules of dimethyl ether and thereby form the dimethoxyethane.
2. The method of claim 1, wherein the silver nano catalyst is supported on an oxide of zirconium and/or an oxide of titanium.
3. The method of any of claims 1 and 2, wherein the silver nano catalyst comprises one or more of: Ag nano/ZrO₂ and 1% Ag nano/TiO₂.
4. The method of claim 1, wherein the silver nano catalyst is supported on alumina.
5. The method of any of claims 1 to 4, wherein the reaction conditions comprise a temperature in a range of 250 °C to 300 °C.
6. The method of any of claims 1 to 5, wherein the reaction conditions comprise a pressure of 15 atm to 25 atm.
7. The method of any of claims 1 to 6, wherein the reaction conditions comprise a GHSV of 6000 to 10000 h⁻¹.
8. The method of any of claims 1 to 7, wherein the silver nano catalyst comprises an average particle size in a range of 1 to 100 nm.
9. The method of any of claims 1 to 8, wherein the molecules of dimethyl ether are in vapor phase during the contacting.
10. The method of any of claims 1 to 9, wherein the contacting is carried out in a fixed bed flow reactor.

11. The method of any of claims 1 to 10, wherein the silver nano catalyst is prepared in a process comprising:
 - reducing Ag^+ ions in a polyvinylpyrrolidone/ethylene glycol solution to form a Ag^+ /polyvinylpyrrolidone/ethylene glycol solution;
 - adding one or more of TiO_2 , ZrO_2 , and alumina to the Ag^+ /polyvinylpyrrolidone/ethylene glycol solution to form the silver nano catalyst, wherein the silver nano catalyst is supported on one or more of TiO_2 , ZrO_2 , and alumina; and
 - drying the silver nano catalyst.
12. The method of claim 11, wherein the reducing of Ag^+ ions is carried out in the polyvinylpyrrolidone/ethylene glycol solution at a temperature in a range of 170 °C to 190 °C.
13. The method of any of claims 11 and 12, wherein the adding of the one or more of TiO_2 , ZrO_2 , and alumina is carried out by incipient wetness impregnation.
14. The method of any of claims 11 to 13, wherein the drying is carried out at a temperature of 110 °C to 130 °C.
15. The method of any of claims 11 to 13, wherein the drying is carried out in a period of 6 to 24 hours.

**FIG. 1**

**FIG. 2****FIG. 3**

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2019/057488

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01J23/50 B01J37/02 B01J37/16 C07C41/14 C07C43/10
ADD.

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)

B01J C07C

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)

EP0-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	YU L ET AL: "Catalytic Oxidation of Dimethyl Ether to Hydrocarbons over SnO₂/MgO and SnO₂/CaO Catalysts", JOURNAL OF NATURAL GAS CHEMISTRY, ELSEVIER, US, CN, vol. 16, no. 2, 1 June 2007 (2007-06-01), pages 200-203, XP022936844, ISSN: 1003-9953, DOI: 10.1016/S1003-9953(07)60048-6 [retrieved on 2007-06-01] page 200, right-hand column, paragraph 2.1 Catalyst preparation - page 201, right-hand column; table 1 ----- -/--	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

20 December 2019

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07/02/2020

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Beckmann, Oliver

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2019/057488

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Week 200728 Thomson Scientific, London, GB; AN 2007-284498 XP002796634, -& CN 1 836 775 A (UNIV GUANGDONG TECHNOLOGY) 27 September 2006 (2006-09-27) abstract	1-15
A	----- HIROSHI YAGITA ET AL: "Oxidative dimerization of dimethyl ether with solid catalysts", APPLIED CATALYSIS, vol. 53, no. 1, 1 January 1989 (1989-01-01), pages 5-9, XP055654600, NL ISSN: 0166-9834, DOI: 10.1016/S0166-9834(00)80002-0 page L5 - page L6; table 1 -----	1-15
A	----- CHIMENTAO R J ET AL: "Synthesis, characterization and catalytic activity of metal nanoparticles in the selective oxidation of olefins in the gas phase", JOURNAL OF EXPERIMENTAL NANOSCIENCE, TAYLOR & FRANCIS LTD., GB, vol. 1, no. 1-4, 1 March 2006 (2006-03-01) , pages 399-418, XP009128048, ISSN: 1745-8080 page 401, paragraph 2.1.; figure 1 -----	11-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2019/057488

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 1836775	A	27-09-2006	NONE
