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Published:

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— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

(88) Date of publication of the international search report:
6 May 2016

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(54) Title: METHANOL PRODUCTION CATALYST AND METHANOL PRODUCTION PROCESS

(57) Abstract: The invention provides a process for producing methanol. The process comprises contacting a gas phase with a solid catalyst, wherein the gas phase comprises (a) H_2 and (b) $C0_2$, CO or a mixture of $C0_2$ and CO, and the catalyst comprises heterometallic particles comprising palladium and zinc. The invention also provides a catalyst which comprises heterometallic particles of palladium and zinc and a support material comprising zinc oxide. Also provided is a process for producing such a catalyst, the process comprising reducing a composition comprising palladium and zinc oxide. A catalyst obtainable by this process is also provided. The invention also relates to uses of the described catalysts for the hydrogenation of $C0_2$, CO, or a mixture of $C0_2$ and CO, to produce methanol, and, more particularly, for the hydrogenation of $C0_2$ to produce methanol. The invention also provides a composition which comprises palladium, zinc oxide and a compound suitable for promoting the reduction by hydrogen gas of zinc oxide to zinc metal.

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2015/052226

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J23/60 B01J27/057 B01J35/00 C07C29/157
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)
EPO-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	US 6 413 449 B1 (WIELAND STEFAN [DE] ET AL) 2 July 2002 (2002-07-02) claim 1	1-43
X	CHEOL-HYUN KIM ET AL: "The Preparation and Characterisation of Pd-ZnO Catalysts for Methanol Synthesis", TOPICS IN CATALYSIS, KLUWER ACADEMIC PUBLISHERS-PLENUM PUBLISHERS, NE, vol. 22, no. 3-4, 1 April 2003 (2003-04-01), pages 319-324, XP019291933, ISSN: 1572-9028 Results and discussion; page 320, left-hand column - right-hand column	1-56

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"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)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
11 March 2016	21/03/2016

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Zieba, Roman

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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB2015/052226

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☒ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

44-56

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☒ No protest accompanied the payment of additional search fees.

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	LIANG X L ET AL: "Carbon nanotube-supported Pd-ZnO catalyst for hydrogenation of CO2 to methanol", APPLIED CATALYSIS B: ENVIRONMENTAL, ELSEVIER, AMSTERDAM, NL, vol. 88, no. 3-4, 20 May 2009 (2009-05-20) , pages 315-322, XP026085599, ISSN: 0926-3373, DOI: 10.1016/J.APCATB.2008.11.018 [retrieved on 2008-11-24] page 316, left-hand column - right-hand column figures 5,9	1-27, 29-56
X	LEBARBIER V ET AL: "The effect of PdZn particle size on reverse-watergas-shift reaction", APPLIED CATALYSIS A: GENERAL, ELSEVIER SCIENCE, AMSTERDAM, NL, vol. 379, no. 1-2, 15 May 2010 (2010-05-15), pages 3-6, XP027013153, ISSN: 0926-860X [retrieved on 2010-03-01] table 1	1-43
X	US 6 342 538 B1 (MATSUMURA YASUYUKI [JP] ET AL) 29 January 2002 (2002-01-29) example 1	1-43
X	US 2007/161717 A1 (HU JIANLI [US] ET AL) 12 July 2007 (2007-07-12) column 37	1-43
X	US 4 393 144 A (ICHIKAWA MASARU [JP]) 12 July 1983 (1983-07-12) example 1	1-43
A	US 2006/182997 A1 (YAMAMOTO TAKAO [JP] ET AL) 17 August 2006 (2006-08-17) paragraph [0002]	45-56
A	US 2011/250122 A1 (JOO SANG HOON [KR] ET AL) 13 October 2011 (2011-10-13) claims 7,23	45-56

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2015/052226

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FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-43

   A process for producing methanol, which process comprises contacting a gas phase with a solid catalyst, wherein the gas phase comprises H2 and CO2, CO or a mixture of CO2 and CO; and the catalyst comprises heterometallic particles, wherein each of the heterometallic particles comprises palladium and zinc.

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2. claims: 44-56

   A catalyst which comprises a support material comprising zinc oxide and heterometallic particles, wherein each of the heterometallic particles comprises palladium and zinc.

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3. claims: 57-71

   A process for producing a catalyst which comprises a support material comprising zinc oxide and heterometallic particles, wherein each of the heterometallic particles comprises palladium and zinc, which process comprises reducing a composition comprising palladium and a support material which comprises zinc oxide.

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4. claims: 72, 73

   Use of the catalyst defined by claims 44-71 for the hydrogenation of CO2, CO, or a mixture of CO2 and CO to produce methanol.

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5. claims: 74-81

   A composition which comprises palladium, zinc oxide, and a compound suitable for promoting the reduction by hydrogen gas of zinc oxide to zinc metal.
