



(43) International Publication Date
25 June 2015 (25.06.2015)

(10) International Publication Number
WO 2015/092006 A3

(51) International Patent Classification:

B01J 23/00 (2006.01) **B01J 35/00** (2006.01)
B01J 23/755 (2006.01) **B01J 37/16** (2006.01)
B01J 23/78 (2006.01) **B01J 37/08** (2006.01)
B01J 23/38 (2006.01) **C07C 1/04** (2006.01)

(21) International Application Number:

PCT/EP2014/078843

(22) International Filing Date:

19 December 2014 (19.12.2014)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

13199164.8 20 December 2013 (20.12.2013) EP

(71) Applicants: **BASF SE** [DE/DE]; 67056 Ludwigshafen (DE). **L'AIR LIQUIDE, SOCIETE ANONYME POUR L'ETUDE ET L'EXPLOITATION DES PROCEDES GEORGES CLAUDE** [FR/FR]; 75, Quai d'Orsay, F-75007 Paris (FR).

(72) Inventors: **HAAS, Andreas**; Eichelsheimer Straße 37-41, 68163 Mannheim (DE). **MILANOV, Andrian**; Rheindammstraße 60, 68163 Mannheim (DE). **URTEL, Heiko**; Nibelungenstraße 2, 67240 Bobenheim-Roxheim (DE). **ODERMATT, Peter**; Kanalstr. 34, 67098 Bad Dürkheim (DE). **SCHWAB, Ekkehard**; Berwartsteinstr. 4, 67434 Neustadt (DE). **HACKEL, Marius**; Gustav-Blum-Strasse 13, 61250 Usingen (DE). **HERRLETT, Ute**; Niederwiesenring 36, 63110 Rodgau (DE). **KRIER, Claudia**; Christian-Stock-Strasse 32, 64319 Pfungstadt (DE). **SCHMITT, Nathalie**; Höhenstrasse 7, 65824 Schwalbach (DE). **WALTER, Stefan**; Am alten Bahndamm 6, 64347 Griesheim (DE).

(74) Agent: **MAIWALD PATENTANWALTS GMBH**; Elisenstr. 3 / Elisenhof, 80335 Munich (DE).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- 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:

13 August 2015

(54) Title: TWO-LAYER CATALYST BED

(57) Abstract: The present invention relates to a catalyst bed comprising a first catalyst layer and a second catalyst layer, wherein the first catalyst layer comprises a first catalyst or precursor thereof active or activatable at a temperature below 340°C; and the second catalyst layer comprises a second catalyst precursor, wherein the second catalyst precursor comprises nickel in Ni(II) form and is activatable to a second catalyst comprising nickel in Ni(0) form at a temperature above 360°C, wherein the second catalyst has an average lateral compression strength after 500 h at a temperature of 650°C of at least 30 N.



WO 2015/092006 A3

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/078843

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	B01J23/00 B01J37/16	B01J23/755 B01J37/08
	B01J23/78 C07C1/04	B01J23/38 B01J35/00
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		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2013/116351 A1 (QUERNER CLAUDIA [DE] ET AL) 9 May 2013 (2013-05-09) cited in the application examples paragraphs [0013], [0135] - [0136] -----	1-5,8,9, 12-14
X	MA ET AL: "Alternative catalyst bed configurations for the autothermic conversion of methane to hydrogen", APPLIED CATALYSIS A: GENERAL, ELSEVIER SCIENCE, AMSTERDAM, NL, vol. 138, no. 2, 9 May 1996 (1996-05-09), pages 265-273, XP022250771, ISSN: 0926-860X, DOI: 10.1016/0926-860X(95)00300-2 par. "Experimental" ----- -/-	1-3,8,9
☒ Further documents are listed in the continuation of Box C. ☒ 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 18 March 2015		Date of mailing of the international search report 17/06/2015
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Omegna, Anna

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/078843

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2004/015031 A1 (MESSENGER BRIAN EDWARD [GB]) 22 January 2004 (2004-01-22) figure 1 paragraphs [0043], [0069] -----	1-3,8,9
X	WO 2012/131318 A1 (JOHNSON MATTHEY PLC [GB]; FARNELL PETER WILLIAM [GB]; FOWLES MARTIN [G]) 4 October 2012 (2012-10-04) claims page 4, line 20 - page 5, line 18 page 7, line 18 - line 23 page 8, line 9 - line 20 page 8, line 30 - page 9, line 3 figure 1 -----	1-5,8,9
X	EP 0 028 835 A1 (VEG GASINSTITUUT NV [NL]) 20 May 1981 (1981-05-20) page 6, line 10 - page 7, line 4 examples figure 1 -----	1-5,8,9, 12-14
X	GB 2 280 618 A (EXXON CHEMICAL PATENTS INC [US]) 8 February 1995 (1995-02-08) abstract page 2, line 8 - line 15 last sentence; page 7 page 12, line 23 - page 13, line 12 page 14, line 8 - line 20 examples figure 1 claims -----	1-5,8,9

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2014/078843

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.:
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.:

1-5, 12-14(completely); 8, 9(partially)

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.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

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

1. claims: 1-5, 12-14(completely); 8, 9(partially)

Catalyst bed (claim 1), process for activating the second catalyst precursor in a catalyst bed by applying a flow of synthesis gas at a temperature below 340°C (claim 4), activated catalyst bed obtainable by that process (claim 8, part), reaction system comprising the catalyst bed (claim 9, part), process for providing CH₄ by feeding synthesis gas to that reaction system (claim 12)

2. claims: 6, 7, 10, 11(completely); 8, 9(partially)

Process for activating the second catalyst precursor in a catalyst bed as defined in claims 1-3 by applying a flow of reaction gas comprising CH₄ and H₂O at a temperature above 360°C (claim 6), activated catalyst bed obtainable by that process (claim 8, part), reaction system comprising the catalyst bed (claim 9, part), process for providing CO and H₂ by feeding a reaction gas comprising CH₄ and H₂O to that reaction system (claim 10)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2014/078843

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2013116351	A1	09-05-2013	NONE

US 2004015031	A1	22-01-2004	AR 029705 A1 10-07-2003
		AU 7433801 A 21-01-2002	
		AU 2001274338 B2 22-12-2005	
		BR 0112469 A 29-07-2003	
		CA 2414186 A1 17-01-2002	
		CN 1441758 A 10-09-2003	
		CN 1690029 A 02-11-2005	
		CZ 20030061 A3 16-04-2003	
		EG 22541 A 31-03-2003	
		EP 1299331 A1 09-04-2003	
		JP 2004502836 A 29-01-2004	
		KR 20030015375 A 20-02-2003	
		MX PA03000302 A 05-04-2004	
		MY 140050 A 30-11-2009	
		NO 20030163 A 27-02-2003	
		PL 358722 A1 09-08-2004	
		TW 567181 B 21-12-2003	
		US 2004015031 A1 22-01-2004	
		WO 0204389 A1 17-01-2002	
		ZA 200210393 A 13-11-2003	

WO 2012131318	A1	04-10-2012	GB 2503152 A 18-12-2013
		WO 2012131318	A1 04-10-2012

EP 0028835	A1	20-05-1981	DE 3063371 D1 07-07-1983
		EP 0028835	A1 20-05-1981
		JP S5682888	A 06-07-1981
		NL 7908283	A 01-06-1981

GB 2280618	A	08-02-1995	NONE
