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- (71) Applicant (for all designated States except US): OX-FORD CATALYSTS LIMITED [GB/GB]; 115e Milton Park, Oxford OX14 4RZ (GB).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): DALY, Francis [US/US]; 701 Old Augusta Road, Waldoboro, ME 04572 (US). RICHARD, Laura [GB/GB]; 4 Hadland Road, Abingdon OX14 3XW (GB). RUGMINI, Sreekala [IN/GB]; 54 Bowmont Water, Didcot OX11 7GF (GB).

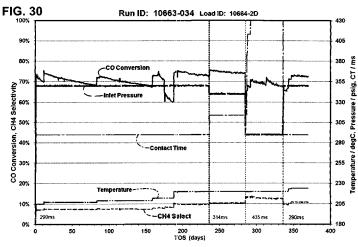
- (74) Agents: JAMES, Anthony Christopher W.P. et al.; Carpmaels & Ransford, One Southampton Row, London WC1B 5HA (GB).
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Published:

- 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))

[Continued on next page]

(54) Title: FISCHER-TROPSCH CATALYSTS AND METHOD OF PREPARATION THEREOF



(57) Abstract: The invention relates to improvements in the design of Fischer-Tropsch catalysts comprising a support and cobalt on the support. A first aspect is the modification of the silica support with at least 11 wt% titania to prevent the formation of cobalt silicates, thereby limiting the deactivation resulting from the silicate formation. A second aspect is the provision of C0₃O₄ particles highly dispersed on the catalyst support with an average particle diameter of the cobalt oxide particle of less than 12 nm in order to improve catalytic activity and selectivity. A third aspect is the deposition of the catalyst precursor on the support by contact with a solution or suspension comprising the catalyst metal precursors and a carboxylic acid, preferably an alpha-hydroxy carboxylic acid in order to minimize the fracturing and fragmentation of the catalyst precursor during the following steps of drying and calcining, thereby preventing the formation of smaller catalyst particles, which should be removed by screening in order to limit pressure drop in the reactor.







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PCT/GB2012/000125 A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J23/75 B01J23/76 ÎNV. B01J23/889 B01J37/02 B01J37/18 B01J21/08 C10G2/00 B01J23/89 B01J35/00 B01J21/06 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 C10G 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 Relevant to claim No. Category* Citation of document, with indication, where appropriate, of the relevant passages US 5 397 806 A (SOLED STUART L [US] ET AL) 1,5-8, Χ 14 March 1995 (1995-03-14) 27,44-47 abstract column 1, lines 12-15 column 9, lines 5-9 example 1 examples 1,2 -/--Х Further documents are listed in the continuation of Box C. See patent family annex. Special categories of cited documents "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 "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 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive 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 step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be special reason (as specified) considered to involve an inventive step when the document is combined with one or more other such documents, such combination "O" document referring to an oral disclosure, use, exhibition or other being obvious to a person skilled in the art document published prior to the international filing date but later than the priority date claimed "&" document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 8 August 2012 26/10/2012 Authorized officer 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 Gosselin, Daniel

International application No PCT/GB2012/000125

C(Continua	tion). DOCUMENTS CONSIDERED TO BE RELEVANT	1
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HINCHIRANAN ET AL: "Ti02 promoted Co/Si02 catalysts for Fischer-Tropsch synthesis", FUEL PROCESSING TECHNOLOGY, ELSEVIER BV, NL, vol. 89, no. 4, 11 December 2007 (2007-12-11), pages 455-459, XP022540761, ISSN: 0378-3820, DOI: 10.1016/J.FUPROC.2007.11.007 the whole document more particularly: "4. Conclusions"	1-8,27, 44-47
X	US 2009/305881 A1 (SIETSMA JELLE RUDOLF ANNE [NL] ET AL) 10 December 2009 (2009-12-10) paragraphs [0027], [0028], [0034] - [0036], [0041] - [0045], [0053], [0054], [0061] examples 1-4,6 tables 4,6,10	9-27, 44-47
Х	WO 2010/097754 A2 (SASOL TECH PTY LTD [ZA]; TERORDE ROBERT JOHAN ANDREAS MARIA [NL]; KRAM) 2 September 2010 (2010-09-02) the whole document	9-27, 31-42, 44-47
X,P	& US 2011/301024 A1 (TERORDE ROBERT JOHAN ANDREAS MARIA [NL] ET AL) 8 December 2011 (2011-12-08) abstract paragraphs [0010] - [0012], [0027], [0030] - [0034], [0039], [0049], [0063] - [0065], [0074], [0082] examples 2-5,7,9,10 tables 1-4 claims	9-27, 31-42, 44-47
X	US 2005/026776 A1 (YAMADA MUNEYOSHI [JP] ET AL) 3 February 2005 (2005-02-03) paragraphs [0015] - [0021], [0026]; examples 1,3-6 table 1 claims	9-27, 31-42, 44-47
X	US 2011/028575 A1 (VAN DE LOOSDRECHT JAN [ZA] ET AL) 3 February 2011 (2011-02-03) paragraphs [0009] - [0018], [0021] - [0022], [0027], [0030] examples tables claims	10-27, 31-42, 44-47

International application No
PCT/GB2012/000125

C(Continua	tion). DOCUMENTS CONSIDERED TO BE RELEVANT	•
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2007/068731 A1 (SHELL INT RESEARCH [NL]; DOGTEROM RONALD JAN [NL]; MESTERS CAROLUS MAT) 21 June 2007 (2007-06-21) page 4, lines 1-27 page 5, lines 10-23 page 7, lines 1-10 page 7, line 30 - page 8, line 2 page 8, line 32 - page 9, line 9 page 11, line 24 - page 12, line 5 page 20, lines 12-30	41-47
X	US 2009/293359 A1 (SIMMONS WAYNE W [US] ET AL) 3 December 2009 (2009-12-03) paragraphs [0159], [0160], [0164] - [0166], [0170], [0175], [0176], [0182] - [0184] claims	31-42, 44-47
X	WO 01/83108 A1 (SHELL INT RESEARCH [NL]; LEDNOR PETER WILLIAM [NL]; NIESEN GERARDUS PE) 8 November 2001 (2001-11-08) page 2, line 22 - page 3, line 2 page 7, line 31 - page 8, line 7 page 11, lines 6-17 examples	31-42, 44-47

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INTERNATIONAL SEARCH REPORT

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:
Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:
2. X Claims Nos.: 28-30 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: See FURTHER INFORMATION sheet PCT/ISA/210
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. X 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.:
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 procified in the invitation.
fee was not paid within the time limit specified in the invitation. X 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: 1-9(completely); 27, 44-47(partially)

cobalt catalyst precursor comprising a titania-modified silica support

2. claims: 9-26(completely); 27, 44-47(partially)

cobalt oxide catalyst precursor wherein the average particle diameter of the cobalt oxide is less than 12 nm as determined by XRD

3. claims: 31-43(completely); 44-47(partially)

for preparing a catalyst precursor; catalytic entities and support not specified

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 28-30

The subject-matter of claims 28, 29, 30 and 44 to 47 as far as it refers to said claims is so vague that it is not possible to identify parameters (composition, structure of the catalyst, Fischer-Tropsch process steps), which could be compared with the products and Fischer-Tropsch processes of known in the art. See Item VIII-3 to VIII-3c.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.2), should the problems which led to the Article 17(2) declaration be overcome.

Information on patent family members

International application No
PCT/GB2012/000125

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