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(54) **CARBON SUPPORTED COBALT AND MOLYBDENUM CATALYST AND USE THEREOF FOR PRODUCING LOWER ALCOHOLS**

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See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,177,203	A	12/1979	Kolbel et al.	
4,752,622	A	6/1988	Stevens	
4,882,360	A	11/1989	Stevens	
5,780,381	A	7/1998	Wilson et al.	
7,375,055	B2	5/2008	Van Berge et al.	
7,396,798	B2	7/2008	Ma et al.	
2008/0280754	A1 *	11/2008	Toledo Antonio	B01J 23/85 502/177
2014/0135411	A1	5/2014	Karim et al.	

FOREIGN PATENT DOCUMENTS

CN	1631527	A	6/2005
CN	101664682	A	3/2010
CN	101733135	A	6/2010
EP	0119609	A1	9/1984
EP	0172431	A2	2/1986
JP	H05-135772	A	6/1993
JP	2011-029171	A	2/2011
WO	WO-03/041860	A2	5/2003
WO	WO-03/076074	A1	9/2003
WO	WO-2009/032982	A2	3/2009
WO	WO-2010/02618	A1	1/2010
WO	WO-2010/098668	A2	9/2010
WO	WO-2011/003884	A1	1/2011
WO	WO 2012/078277	*	6/2012
WO	WO-2012/143131	A1	10/2012
WO	WO-2013/007345	A1	1/2013

OTHER PUBLICATIONS

International Preliminary Report on Patentability issued by the International Bureau on Oct. 22, 2013 for PCT/EP2012/001699 filed Apr. 19, 2012 and published as WO 2012/143131 on Oct. 26, 2012 (Applicants—Saudi Basic Industries Corporation, et al.; Inventors—Karim, et al.) (5 pages).

International Search Report mailed by the International Bureau on Jul. 17, 2013 for PCT/EP2012/001699 filed Apr. 19, 2012 and published as WO 2012/143131 on Oct. 26, 2012 (Applicants—Saudi Basic Industries Corporation, et al.; Inventors—Karim, et al.) (2 pages).

Written Opinion mailed by the International Bureau on Jul. 17, 2013 for PCT/EP2012/001699 filed Apr. 19, 2012 and published as WO 2012/143131 on Oct. 26, 2012 (Applicants—Saudi Basic Industries Corporation, et al.; Inventors—Karim, et al.) (4 pages).

Preliminary Amendment filed Sep. 19, 2013 for U.S. Appl. No. 14/006,199, filed Jan. 31, 2014 and published as U.S. 2014/0135411 on May 15, 2014 (Applicants—Saudi Basic Industries Corporation, et al.; Inventors—Karim, et al.) (3 pages).

Preliminary Amendment filed Nov. 25, 2013 for U.S. Appl. No. 14/006,199, filed Jan. 31, 2014 and published as U.S. 2014/0135411 on May 15, 2014 (Applicants—Saudi Basic Industries Corporation, et al.; Inventors—Karim, et al.) (5 pages).

Auer (1998) Carbons as supports for industrial precious metal catalysts. Applied Catalysis A: General, 173: 259-271.

Bao J, et al. (2003) A highly active K-Co-Mo/C catalyst for mixed alcohol synthesis from Co + H2. Chemical Communications, 9(6): 746-747.

Commereuc (1980) Catalytic synthesis of low molecular weight olefins from CO; and H2 with Fe (CO)5, FE3(CO)12, and [HFe3(CO)11]—supported on inorganic oxides. J. Chem. Soc., Chem. Commun.: 154-155.

Dry (2004) Chapter 3—Chemical concepts used for engineering purposes. Stud. Surf. Sci. Catal, 152: 196-257.

(Continued)

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(57) **ABSTRACT**

The present invention relates to a method for preparing a catalyst composition comprising cobalt and molybdenum on a carbon support, characterized in that the cobalt- and molybdenum-source are dissolved in an organic solvent that is miscible with water. Moreover, a carbon supported cobalt molybdenum catalyst composition obtainable by said method and a process for producing alcohols from syngas using said carbon supported cobalt molybdenum catalyst composition is provided.

9 Claims, No Drawings