US009409153B2

(12) **United States Patent**
Yang et al.

(10) **Patent No.: US 9,409,153 B2**
(45) **Date of Patent: Aug. 9, 2016**

(54) **SUPPORTED MO—O—K—ME$_x$O$_y$ CATALYST FOR THE SYNTHESIS OF METHANETHIOL FROM HIGH H$_2$S-CONTAINING SYNGAS**

(75) Inventors: **Yiquan Yang**, Xiamen (CN); **Yingjuan Hao**, Xiamen (CN); **Aiping Chen**, Xiamen (CN); **Qi Wang**, Xiamen (CN); **Lingmei Yang**, Xiamen (CN); **Qiaoling Li**, Xiamen (CN); **Shenjun Dai**, Xiamen (CN); **Weiping Fang**, Xiamen (CN); **Jan-Olaf Barth**, Frankfurt (DE); **Christoph Weckbecker**, Gruendau-Lieblos (DE); **Klaus Huthmacher**, Gelnhausen (DE)

(73) Assignee: **EVONIK DEGUSSA GMBH**, Essen (DE)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 584 days.

(21) Appl. No.: **12/810,688**

(22) PCT Filed: **Nov. 28, 2008**

(86) PCT No.: **PCT/EP2008/066451**
§ 371 (c)(1),
(2), (4) Date: **Jun. 25, 2010**

(87) PCT Pub. No.: **WO2009/083368**
PCT Pub. Date: **Jul. 9, 2009**

(65) **Prior Publication Data**

US 2010/0286448 A1 Nov. 11, 2010

(30) **Foreign Application Priority Data**

Dec. 28, 2007 (CN) 2007 1 0305947

(51) **Int. Cl.**

B01J 21/08	(2006.01)
B01J 23/04	(2006.01)
B01J 23/28	(2006.01)
B01J 23/88	(2006.01)
B01J 23/882	(2006.01)
B01J 23/883	(2006.01)
B01J 23/00	(2006.01)
B01J 23/887	(2006.01)
B01J 37/02	(2006.01)
B01J 37/16	(2006.01)
C07C 319/02	(2006.01)
B01J 21/06	(2006.01)

(52) **U.S. Cl.**
CPC ***B01J 23/28*** (2013.01); ***B01J 23/002*** (2013.01); ***B01J 23/8872*** (2013.01); ***B01J 37/0207*** (2013.01); ***B01J 37/16*** (2013.01); ***C07C 319/02*** (2013.01); *B01J 21/063* (2013.01); *B01J 2523/00* (2013.01)

(58) **Field of Classification Search**
CPC C07C 319/06; B01J 21/06; B01J 23/28; B01J 21/08; B01J 23/8872; B01J 37/027; B01J 37/16; B01J 2523/13; B01J 2523/68; C23C 18/16; C23C 18/54
USPC 502/73, 211, 243, 302, 303, 304, 309, 502/313, 315, 316, 317
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

7,247,376	B1 *	7/2007	Chen et al.	428/403
2007/0213564	A1	9/2007	Yang et al.	

FOREIGN PATENT DOCUMENTS

CN	1207957	2/1999
CN	1207958	2/1999
CN	1528515	9/2004
CN	1528516	9/2004
CN	1559676 A	1/2005
EP	0 167 354	1/1986
JP	2007-508256	4/2007
JP	2007-119900	5/2007
WO	2005/040082	5/2005

OTHER PUBLICATIONS

International Search Report for PCT/EP2008/066451 mailed Nov. 23, 2009.
Chen et al., "Direct synthesis of methanethiol from H$_2$S-rich syngas over sulfided Mo-based catalysts", Journal of Molecular Catalysis A, Chemical, vol. 283, No. 1-2, 2007, pp. 69-76.
Chen et al., "Catalytic Synthesis of Methanethiol from H$_2$S-rich Syngas Over Sulfided SiO$_2$-suported Mo-based Catalysts", Catalysts Letters, vol. 12, No. 3-4, 2007, pp. 260-265.
Henry et al., "Electroless (Autocatalytic) Plating", Metal Finishing, vol. 105, No. 10, 2007, pp. 350-356.
Liu et al., "The effect of acetic acid pretreatment for cobalt catalysts prepared from cobalt nitrate", Catalysis Communications, vol. 8, No. 5, 2007, pp. 773-776.

(Continued)

Primary Examiner — Jun Li
(74) *Attorney, Agent, or Firm* — Smith, Gambrell & Russell, LLP

(57) **ABSTRACT**

This invention is related to a preparation method of a supported catalyst Mo—O—K-Me$_x$O$_y$ for the synthesis of methanethiol from H$_2$S-containing syngas. The catalyst comprises of an active component of Mo—O—K-based species, an active promoter and a support denoted as metal (or metals)-carrier. The support is prepared by electroless plating method in such a way that the metal or metals chosen are plated onto the surface of the carrier. Transition metal, especially Fe, Co or Ni are selected to be the plating metal, while SiO$_2$, Al$_2$O$_3$ or TiO$_2$ are selected to be carrier. The catalyst thus prepared is found to be efficient for the synthesis of methanethiol from H$_2$S-containing syngasor carbon oxides/hydrogen mixtures, especially regarding a minor formation of the by-product CO$_2$.

12 Claims, No Drawings