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2012 年 11 月 1 日 (01.11.2012)



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B01J 23/72 (2006.01) C07C 31/20 (2006.01)
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B01J 23/88 (2006.01)

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(81) 指定国 (除另有指明, 要求每一种可提供的国家保护): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, 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) 指定国 (除另有指明, 要求每一种可提供的地区保护): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), 欧亚 (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), 欧洲 (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, ML, MR, NE, SN, TD, TG)。

根据细则 4.17 的声明:

— 发明人资格(细则 4.17(iv))

本国际公布:

— 包括国际检索报告(条约第 21 条(3))。

(88) 国际检索报告公布日期: 2012 年 11 月 22 日

(54) Title: HYDROGENATED ALKYL OXALATE COMPOSITE CARRIER CATALYST FOR SYNTHESIZING ETHYLENE GLYCOL AND PREPARATION METHOD THEREFOR

(54) 发明名称: 草酸烷基酯加氢合成乙二醇用复合载体催化剂及制备方法

(57) Abstract: The present invention relates to a hydrogenated alkyl oxalate composite carrier catalyst for synthesizing ethylene glycol and preparation method therefor. The chemical formula of the composite carrier catalyst is CuO/ROx-MOy, the percentage by mass of CuO being 5% to 60%, the percentage by mass of ROx being 10% to 90%, the percentage by mass of MOy being 0.1% to 60%, x being 1/2 of the highest valence of R, y being 1/2 of the highest valence of M, R being chosen from one of Si, Al, Zr, or Ti, and M being chosen from one of Si, Al, Cr, Zr, Ti, B, Zn, Mo, Ce, Bi, or La. Compared to the prior art, the hydrogenated alkyl oxalate catalyst for synthesizing ethylene glycol uses a composite carrier that effectively disperses the active ingredient, copper, so that copper crystal grains are not easily sintered, thereby enhancing the service life of the catalyst. The composite carrier also effectively adjusts the surface acidity and alkalinity, reduces byproduct generation, and enhances the selectivity of ethylene glycol. The total conversion rate of oxalic ester exceeds 99.9%, and the selectivity of ethylene glycol is greater than 95%. The present invention can be applied in the industrial production of ethylene glycol.

(57) 摘要: 本发明涉及一种草酸烷基酯加氢合成乙二醇用复合载体催化剂及其制备方法, 该复合载体催化剂的化学式为 CuO/ROx-MOy, CuO 质量百分含量为 5%-60%, ROx 质量百分含量为 10%-90%, MOy 质量百分含量为 0.1%-60%, x 为 R 最高价态的 1/2, y 为 M 最高价态的 1/2, R 选自 Si、Al、Zr、Ti 的一种, M 选自 Si、Al、Cr、Zr、Ti、B、Zn、Mo、Ce、Bi、La 的一种。与现有技术相比, 本发明中草酸烷基酯加氢合成乙二醇的催化剂采用复合载体, 该类型载体能有效的分散活性组分铜, 使铜晶粒不易烧结, 提高催化剂的使用寿命。同时复合载体能有效的调节催化剂表面酸碱性, 减少副产物的生成, 提高乙二醇选择性。草酸酯总转化率达 99.9% 以上, 乙二醇选择性大于 95%。本发明可用于乙二醇的工业生产中。

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2012/074092

A. CLASSIFICATION OF SUBJECT MATTER

See the extra sheet

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)

IPC: 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)

CNKI, CNPAT, CNTXT, WPI, EPODOC, ISI WEB OF KNOWLEDGE: alkyl oxalate, oxalate, ethylene glycol, copper oxide, composite carrier, composite (mixed) metal oxide

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 101485984 A (INSTITUTE OF COAL CHEMISTRY, CHINESE ACADEMY OF SCIENCES), 22 July 2009 (22.07.2009), claim 1, and embodiment 5	1-10
X	US 4751005 A (NIPPON SHOKUBAI KAGAKU KOGYO CO., LTD.), 14 June 1988 (14.06.1988), claims 8, 10 and 12	1-2
Y	Description, column 8, line 44 to column 9, line 15	4
PX	CN 102225338 A (PUJING CHEMICAL INDUSTRY (SHA) LTD.), 26 October 2011 (26.10.2011), claims 1-10	1-10
X	CN 101829579 A (SHANGHAI INSTITUTE OF TECHNOLOGY), 15 September 2010 (15.09.2010), claims 1-3	1-3
A	SEKIZAWA, K. et al. Selective removal of CO in methanol reformed gas over Cu-supported mixed metal oxides, APPLIED CATALYSIS A: GENERAL, 1998, vol. 169, pages 291-297	1-10
A	CN 101342489 A (SHANGHAI COKING & CHEMICAL CORP.), 14 January 2009 (14.01.2009), claims 1-10	1-10

☐ 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	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"&" document member of the same patent family
"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	

Date of the actual completion of the international search 03 July 2012 (03.07.2012)	Date of mailing of the international search report 26 July 2012 (26.07.2012)
Name and mailing address of the ISA/CN: State Intellectual Property Office of the P. R. China No. 6, Xitucheng Road, Jimenqiao Haidian District, Beijing 100088, China Facsimile No.: (86-10) 62019451	Authorized officer WANG, Suyan Telephone No.: (86-10) 62084746

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2012/074092

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
CN 101485984 A	22.07.2009	CN 101485984 B	08.12.2010
US 4751005 A	14.06.1988	EP 0257983 A	02.03.1988
		JP 63158189 A	01.07.1988
		EP 0257983 B	25.07.1990
		DE 3763937 G	30.08.1990
		ES 2016363 B	01.11.1990
		JP 3034997 B	24.05.1991
		CA 1301964 C	26.05.1992
		CA 1301965 C	26.05.1992
		JP 1678859 C	13.07.1992
CN 102225338 A	26.10.2011	None	
CN 101829579 A	15.09.2010	CN 101829579 B	23.05.2012
CN 101342489 A	14.01.2009	None	

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2012/074092

CONTINUATION OF SECOND SHEET: A. CLASSIFICATION OF SUBJECT MATTER

B01J 23/76 (2006.01) i

B01J 23/72 (2006.01) i

B01J 23/843 (2006.01) i

B01J 23/88 (2006.01) i

B01J 37/03 (2006.01) i

C07C 31/20 (2006.01) i

C07C 29/149 (2006.01) i

A. 主题的分类

见附加页

按照国际专利分类(IPC)或者同时按照国家分类和 IPC 两种分类

B. 检索领域

检索的最低限度文献(标明分类系统和分类号)

IPC: B01J, C07C

包含在检索领域中的除最低限度文献以外的检索文献

在国际检索时查阅的电子数据库(数据库的名称, 和使用的检索词(如使用))

CNKI, CNPAT, CNTXT, WPI, EPODOC, ISI WEB OF KNOWLEDGE:草酸酯, 草酸烷基酯, 乙二醇, 氧化铜, CuO, 复合载体, 复合金属氧化物, oxalate, ethylene glycol, copper oxide, composite carrier, composite (mixed) metal oxide

C. 相关文件

类 型*	引用文件, 必要时, 指明相关段落	相关的权利要求
X	CN101485984A (中国科学院山西煤炭化学研究所) 22.7 月 2009 (22.07.2009) 权利要求 1 及实施例 5	1-10
X	US4751005A (NIPPON SHOKUBAI KAGAKU KOGYO CO LTD) 14.6 月 1988 (14.06.1988) 权利要求 8、10 和 12	1-2
Y	说明书第 8 栏 44 行-第 9 栏第 15 行	4
PX	CN102225338A(上海浦景化工技术有限公司) 26.10 月 2011 (26.10.2011) 权利要求 1-10	1-10
X	CN101829579A (上海应用技术学院) 15.9 月 2010 (15.09.2010) 权利要求 1-3	1-3
A	Koshi Sekizawa et al. Selective removal of CO in methanol reformed gas over Cu-supported mixed metal oxides, Applied Catalysis A:General, 1998 年, 169 卷, 第 291-297 页	1-10
A	CN101342489A (上海焦化有限公司) 14.1 月 2009 (14.01.2009) 权利要求 1-10	1-10



其余文件在 C 栏的续页中列出。



见同族专利附件。

* 引用文件的具体类型:

“A” 认为不特别相关的表示了现有技术一般状态的文件

“E” 在国际申请日的当天或之后公布的在先申请或专利

“L” 可能对优先权要求构成怀疑的文件, 或为确定另一篇引用文件的公布日而引用的或者因其他特殊理由而引用的文件(如具体说明的)

“O” 涉及口头公开、使用、展览或其他方式公开的文件

“P” 公布日先于国际申请日但迟于所要求的优先权日的文件

“T” 在申请日或优先权日之后公布, 与申请不相抵触, 但为了理解发明之理论或原理的在后文件

“X” 特别相关的文件, 单独考虑该文件, 认定要求保护的发明不是新颖的或不具有创造性

“Y” 特别相关的文件, 当该文件与另一篇或者多篇该类文件结合并且这种结合对于本领域技术人员为显而易见时, 要求保护的发明不具有创造性

“&” 同族专利的文件

国际检索实际完成的日期

03.7 月 2012 (03.07.2012)

国际检索报告邮寄日期

26.7 月 2012 (26.07.2012)

ISA/CN 的名称和邮寄地址:

中华人民共和国国家知识产权局

中国北京市海淀区蓟门桥西土城路 6 号 100088

传真号: (86-10)62019451

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国际检索报告

关于同族专利的信息

国际申请号

PCT/CN2012/074092

检索报告中引用的 专利文件	公布日期	同族专利	公布日期
CN101485984A	22.07.2009	CN101485984B	08.12.2010
US4751005A	14.06.1988	EP0257983A	02.03.1988
		JP63158189A	01.07.1988
		EP0257983B	25.07.1990
		DE3763937G	30.08.1990
		ES2016363B	01.11.1990
		JP3034997B	24.05.1991
		CA1301964C	26.05.1992
		CA1301965C	26.05.1992
		JP1678859C	13.07.1992
CN102225338A	26.10.2011	无	
CN101829579A	15.09.2010	CN101829579B	23.05.2012
CN101342489A	14.01.2009	无	

续：第 2 页，A. 主题的分类

B01J 23/76 (2006.01) i

B01J 23/72 (2006.01) i

B01J 23/843 (2006.01) i

B01J 23/88 (2006.01) i

B01J37/03 (2006.01) i

C07C 31/20 (2006.01) i

C07C 29/149 (2006.01) i