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(54) Title: THE CATALYST AND METHOD OF CATALYTIC REDUCTION OF ESTERS OF HYDROXYCARBOXYLIC ACID TO GLYCOLS

(57) Abstract: The catalyst and method for catalytic reduction of esters of hydroxycarboxylic acids to glycols is disclosed. Esters of hydroxycarboxylic acids are contacted with hydrogen in gas phase at the presence of catalyst which contains mixture of copper and/or oxide of copper and/or hydroxide of copper and/or salt or mixture of salts of copper and of inorganic acids of the element IVb, Va and VIa groups of periodic system, and oxide or mixture of oxides of elements of IVb, Va and VIa groups of periodic system. The process of reduction of esters of hydroxycarboxylic acids to glycols is carried out at hydrogen pressures of less than 10 atm and temperature between 140 and 220°C.



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## **The catalyst and method of catalytic reduction of esters of hydroxycarboxylic acid to glycols**

### FIELD OF THE INVENTION

The present invention relates to a process for the production of diols with high yield and selectivity by hydrogenation of hydroxycarboxylic acid esters in gas phase over copper  
5 containing catalysts. In particular, the present invention relates to a process for the production of ethylene and propylene glycols.

### DESCRIPTION OF RELATED ART

The ethylene and propylene glycols are used in a wide variety of applications such as  
10 monomers in polyester resins; in antifreeze and de-icing fluids; in the manufacture of food, drugs and cosmetic products; and in liquid detergents. Commercial production of glycols is currently petroleum-based and involves the high pressure and high temperature hydrolysis of alkylene oxides.

Since this process starts with ethylene and propylene, the price of the resulting 1,2-diols  
15 depends on the change in the price of oil and other hydrocarbon. The new method is demanded to produce glycols from renewable resources such as plants.

It is well known that plants produce carbohydrates from atmospheric carbon dioxide and sunlight in the process of photosynthesis. Furthermore, as carbon dioxide is a greenhouse gas, so any additional removal of the gas from the atmosphere helps to offset the increase  
20 in this gas by industrial emissions. The method based on hydroxycarboxylic acids obtained by fermentation of crude biomass is promising way for glycols production (WO 2000030744, US 6455742, US 6479713).

It is known that liquid-phase hydrogenation of carboxyl groups occurs under high hydrogen pressure. To perform the hydrogenation process under milder conditions  
25 carboxylic acids are usually converted into more readily reducible esters. Various patents and articles disclose the reduction of hydroxycarboxylic acid esters. For example, the hydrogenation of organic esters to alcohols and glycols in a liquid phase was reported by Adkins and co-workers who were able to achieve 80% yields of propylene glycol from

methyl lactate over copper/chromium oxide and Raney nickel catalysts at temperature from 150° to 250°C and extremely high hydrogen pressures from 20 to 30 MPa (Bowden and Adkins, J. Am. Chem. Soc. 56: 689 (1934); Adkins and Billica, J. Am. Chem. Soc. 70: 3118 (1948); Adkins and Billica, J. Am. Chem Soc. 70: 3121 (1948)).

- 5 In addition to high pressure high catalyst loading is necessary to achieve these relatively high yields. Broadbent et al. (J. Org. Chem. 24: 1847 (1959)) was able to obtain propylene glycol from ethyl lactate over ruthenium black catalysts with yield as high as 80% at 150°C but at very high hydrogen pressure about 25 MPa.

The hydrogenation of organic esters to glycols in a liquid phase was reported by Luo and  
10 co-workers who have achieved 83% yield of propylene glycol from ethyl lactate over Ru-Sn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 150°C and 5.5 MPa. (Luo, G., Yan, S., Qiao, M., Zhuang, J., Fan, K. Appl. Catal. A. 275: 95 (2004)).

The serious disadvantage of all mentioned processes of a liquid phase hydrogenation is necessity to use a high hydrogen pressure.

- 15 Carrying out the process of hydrogenation in a vapor phase allows lowering hydrogen pressure. For example, the hydrogenation of organic esters to alcohols and glycols in a vapor phase over copper-zinc oxides catalysts at 234°C, 1.6 MPa and LHSV=1.06 h<sup>-1</sup> was reported by Bradley and co-workers (Pat. WO8203854, 1982) who have achieved 97.7% selectivity to propylene glycol and 34.7 % conversion of ethyl lactate. The specific  
20 capacity of the catalyst is 0.038 g of propylene glycol /(ml of catalyst\*h).

Despite these efforts, a need for new methods of production of glycols remains that can be performed under relatively mild conditions and which results in high conversion of esters, selectivity to glycols and specific capacity of the catalyst.

## 25 SUMMARY OF THE INVENTION

The present invention provides a process for the low-cost, bulk production of glycols from esters of hydroxycarboxylic acid under relatively mild conditions with high conversion of esters, selectivity to glycols and specific capacity of the catalyst. In more detail, the present

invention provides a process for the production of glycols, which comprises: reacting a mixture of esters of hydroxycarboxylic acid and hydrogen in gas phase at presence of the catalyst which contains mixture of copper and/or oxide of copper and/or hydroxide of copper and/or salt or mixture of salts of copper and of inorganic acids of the element IVb, Va and VIa groups of periodic system, and oxide or mixture of oxides of the element of IVb, Va and VIa groups of periodic system.

Catalyst can be prepared by the reductive thermal treatment of the composition, which contains salt or mixture of salts of copper and of inorganic acids of the element IVb, Va and VIa groups of periodic system and/or mixture of oxide and/or hydroxide of copper and oxides and/or hydroxides of the elements of IVb, Va and VIa groups of periodic system at flow of hydrogen and high temperature (preferable, at temperature between about 350 to 500°C within 1-6 hour). As a result the catalysts have been obtained which contain various amount of copper and oxide of copper (preferable 14-50% wt. of copper and 1-15% wt. oxide of copper).

For the illustration of the method the esters of aliphatic alcohols and lactic and glycolic acids were used as esters of hydroxycarboxylic acid in order to obtain propylene and ethylene glycols correspondingly.

#### EXAMPLES

##### Example 1

The catalyst was prepared by reductive thermal decomposition of mixture of copper silicate (95 %wt.) and copper molybdate (5 %wt.) under flow of hydrogen and temperature about 500°C within 1 hour. As a result the catalyst which contains 47 %wt. of copper and 4 %wt of copper oxide has been obtained. Copper silicate, copper molybdate, molybdenum oxide and silica – the rest.

0.45 g of 0.3-0.5 mm fraction of the catalyst was mixed with 0,45 g and 0.8-1.0 mm fraction of quartz glass and was loaded into the quartz tube U-shaped reactor.

Methyl lactate heated up to temperature of 185°C and hydrogen were fed to mixer with flow rate 0.4 ml/hour and 9 l/hour accordingly. Resulting gaseous mixture of hydrogen and methyl lactate were supplied into reactor. Temperature in the reactor was maintained at

about 200°C. The pressure – 1 atm. Process was carried out within five hours. The products of the reaction were condensed and the condensate was analyzed. The condensate has the following composition, %wt.: methyl lactate – 8.5; methanol – 3.3; 1-hydroxy-2-propanone – 13.0; propylene glycol – 71.3; unidentified by-products – 3.9. The conversion of methyl lactate was 87 %mol., selectivity to propylene glycol was 89 %mol. The specific capacity of the catalyst (g glycol/g catalyst/hour) was 0.56.

Even in 100 hours after starting of the process, the selectivity to propylene glycol was 88%.

#### Example 2-7

10 Processes were performed similarly to an example 1 with various catalysts and under various conditions.

Precursors for preparation of the catalysts, conditions of synthesis of the catalysts, contents of copper and oxides of copper in prepared catalysts are shown in Table 1. Conditions and results of hydrogenation in the presence of the given catalysts are shown in Table 2.

15 Table 1. Conditions of preparation of catalysts

№ catalyst	Precursor (%wt.)	Condition of preparation		Content, % wt.		
		T, °C	Time h	Copper	Oxides of copper	Hydroxide of copper
1	Copper silicate (95) Copper molybdate (5)	450	1	47	4	0
2	Copper silicate (100)	340	4	34	7	2
3	Copper silicate (100)	360	4	39	8	1
4	Copper silicate (100)	400	3	44	5	0.1
5	Copper silicate (90) Copper vanadate (10)	450	2	29	6	3
6	Copper silicate (100)	400	3	50	1	0
7	Copper silicate (85) Copper tungstate (15)	380	6	22	10	2

Table 2. Conditions and results of hydrogenation

№ example	№ catalyst	Esters	Tempe- rature of hydroge- nation	Feeding of esters	Conver- sion of esters	Selecti- vity to glycols	The specific capacity of the catalyst
			□C				ml/h
1	1	Methyl lactate	185	0.4	87	89 (88*)	0.56
2	2	Methyl lactate	200	0.4	93	80 (79*)	0.53
3	3	Methyl lactate	200	0.6	77	74 (72*)	0.61
4	4	Ethyl lactate	200	0.6	97	82 (80*)	0.54
5	5	Ethyl glycolat e	180	0.6	68	90 (89*)	0.42
6	6	Buthyl lactate	200	0.8	93	82 (80*)	0.62
7	7	Buthyl lactate	190	0.4	98	80 (77*)	0.30

Notes:

\* - In parentheses: the value of selectivity obtained after 100 hours of continuous process.

**Claims**

1. The catalyst for catalytic reduction of esters of hydroxycarboxylic acid to glycols, wherein the catalyst contains mixture of copper and/or oxide of copper and/or hydroxide of copper and/or salt or mixture of salts of copper and of inorganic acids of the element IVb, Va and VIa groups of periodic system, and oxide or mixture of oxides of elements of IVb, Va and VIa groups of periodic system.  
5
2. The catalyst for catalytic reduction of esters of hydroxycarboxylic acid to glycols according to claim 1, wherein the catalyst contains 14-50% wt. of copper.
3. The method for preparation of the catalyst according to claim 1, wherein the catalyst is prepared by reductive thermal treatment of the composition, which contains of salt or mixture of salts of copper and of inorganic acids of the element IVb, Va and VIa groups of periodic system and/or mixture of oxide and/or hydroxide of copper and oxides and/or hydroxides of the elements of IVb, Va and VIa groups of periodic system.  
10
4. The method of catalytic reduction of esters of hydroxycarboxylic acid to glycols, comprising contact of esters of hydroxycarboxylic acids with hydrogen in gas phase, wherein the process is carried out at presence of the catalyst according to claim 1.  
15
5. The method according to claim 4, wherein the processes is carried out at pressure below 10 bar and temperature between 140 and 220°C.
6. The method according to claim 4, wherein the processes is carried out at temperature  
20 between 180 and 200°C.

**AMENDED CLAIMS****received by the International Bureau on 14 July 2009 (14.07.09)****Claims**

1. The catalyst for hydrogenation of esters of hydroxycarboxylic acid by hydrogen to glycols, wherein the catalyst contains zero valent copper, one and more salts of copper and inorganic acid of one of the elements 5, 6 and 14 groups of periodic system, one and more  
5 oxides of one of the elements 5, 6 and 14 groups of periodic system and oxide and/or hydroxide of copper.
2. The catalyst for hydrogenation of esters of hydroxycarboxylic acid by hydrogen to glycols according to claim 1, wherein the catalyst contains 14-50% wt. of zero valent copper.
- 10 3. The method for preparation of catalyst according to claim 1, wherein the catalyst is prepared by reductive thermal treatment of the composition, which contains of salt or mixture of salts of copper and of inorganic acids of the element 5, 6 and 14 groups of periodic system.
- 15 4. The method for preparation of glycols, comprising contact of esters of hydroxycarboxylic acids with hydrogen in gas phase, wherein the process is carried out in the presence of the catalyst according to claim 1, at atmospheric pressure and temperature between 180 and 200 C.



INTERNATIONAL SEARCH REPORT

International application No  
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<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
INV.	B01J23/72 B01J23/888	C07C29/147 B01J23/885
	C07C31/20 B01J37/18	B01J23/847 B01J23/88
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
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 practical, search terms used) EPO-Internal, WPI Data		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> 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 document 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. *Z* document member of the same patent family		
Date of the actual completion of the international search  18 May 2009		Date of mailing of the international search report  29/05/2009
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  Schnitzlbaumer, M

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Information on patent family members

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