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(54) Title: PROCESS FOR MANUFACTURE OF ETHYLENE GLYCOL

(57) Abstract: Provided are process for the manufacture of ethylene glycol starting from ethylene oxide (EO) and said process using a reaction mixture comprising EO, a Ti-MWW zeolite and water.

PROCESS FOR MANUFACTURE OF ETHYLENE GLYCOL

The present invention relates to a process for the manufacture of ethylene glycol starting from ethylene oxide (EO).

Ethylene Glycol (Mono-Ethylene Glycol or MEG) is an important organic chemical raw material mainly used in the production of polyester (more precisely of PET or poly-ethylene-terephthalate) and as antifreeze agent.

At present, large-scale ethylene glycol production is generally made using a non-catalytic direct hydration method wherein ethylene oxide (EO) and water are reacted generally in a molar ratio of about 1: 20-22 (molar ratio) resulting in an ethylene glycol aqueous solution containing only about 10% (mass fraction) of MEG, the rest being water and by-products like diethylene glycol (DEG) and triethylene glycol (TEG). Increasing the amount of water used for this method can reduce the by-product formation and improve the conversion rate of ethylene oxide. However, it makes it necessary to set up multiple evaporators/distillation columns, increasing the equipment investment and energy consumption, which directly affects the production cost of ethylene glycol.

Zeolites of the Ti-MWW type are known to be catalysts active in epoxidation reactions: see for instance US6759540 and US7323154.

The inventors have now discovered that this kind of catalysts (zeolite of the Ti-MWW type) is also very active in the synthesis of MEG starting from EO and water (i.e. in the hydrolysis of EO to MEG). Besides activating the reaction, this type of catalyst also allows reducing the amount of water used (typically decreasing the water/EO ratio to about 5:1) in said synthesis hence rendering it more economical and environmentally friendly.

Therefore, the present invention relates to a process for the manufacture of ethylene glycol starting from ethylene oxide (EO), said process using a reaction mixture comprising EO, a Ti-MWW zeolite and water.

Preferred embodiments are those according to which:

- the zeolite is modified with an organic amine, preferably with piperidine or hexamethyleneimine as disclosed in CN101003376;
- the catalyst concentration in the reaction mixture is in the range of from 0.5 to 5 wt. %;
- the process is performed at a temperature from 20°C to 150°C;

- the molar ratio of water to EO is in the range of from 1 to 50.

The use of hydrogen peroxide in the reaction mixture is preferred. In that embodiment:

- the molar ratio of hydrogen peroxide to EO is preferably in the range of from 0.01 to 10; and/or
- the molar ratio of water to hydrogen peroxide is preferably in the range of from 5 to 50.

Considering the fact that EO is extremely flammable and explosive, care should be taken to work in conditions outside the explosion zone.

In a preferred sub-embodiment, when using hydrogen peroxide in the reaction mixture, said mixture also comprises a hydrogen peroxide stabilizer like a mineral acid, preferably nitric acid, and/or HEDP (1-hydroxy ethylidene-1, 1-diphosphonic acid).

In the invention, the catalyst is preferably used as a slurry catalyst or a fixed bed catalyst. Hence, the zeolite is preferably mixed with a binder like silica, alumina or a mixture thereof and then shaped for instance by extrusion.

The following Examples illustrate some embodiments of the present invention.

COMPARATIVE EXAMPLE 1

A hydration reaction (HR) for producing ethylene glycol is carried out under vigorous stirring in an autoclave reactor equipped with a 45 mL Telfon-inner. A TS-1 catalyst (0.1 g, Si/Ti=50), water (5 g) and ethylene oxide (0.44 g) are added into the reactor, and the pressure of the reactor is then raised to 1.5 MPa with nitrogen. The TS-1 catalyst was prepared according to the procedure described in U.S. Pat. No. 4,410,501.The reaction mixture is immediately immersed in a pre-heated oil bath to start the reaction. The reaction mixture is stirred at 40°C for 4 h, and then immediately cooled down in an ice bath to stop the reaction.

Both the gas and the liquid phase samples are collected and analyzed by gas chromatography (GC) using isopropanol as an internal standard. The gases are vented into an acetonitrile solvent for GC analysis. The catalyst is removed from the reaction mixture by centrifugation and the supernatant is analyzed by GC for organic products.

EXAMPLE 2

The hydration reaction is run according to the same procedure as Comparative Example 1 except that a Ti-MWW (0.1 g) is used as a catalyst instead of a TS-1

catalyst. The Ti-MWW was prepared according to a known literature procedure (Chemistry Letters, 2000: 774).

EXAMPLE 3

The hydration reaction is run according to the same procedure as Example 2 except that the Ti-MWW catalyst was chemically treated in an aqueous solution of piperidine according to a known literature procedure (Journal of Physical Chemistry C, 2008, 112, 6132).

EXAMPLE 4

The hydration reaction is run according to the same procedure as Example 2 except that the Ti-MWW catalyst was chemically treated in an aqueous solution of hexamethyleneimine according to a known literature procedure (Journal of Physical Chemistry C, 2008, 112, 6132).

EXAMPLE 5

The hydration reaction is run according to the same procedure as Example 2 except that the amount of Ti-MWW is 0.2 g.

EXAMPLE 6

The hydration reaction is run according to the same procedure as Example 2 except that the amount of water is 2 g.

EXAMPLE 7

The hydration reaction is run according to the same procedure as Example 3 except that the amount of water is 2.7 g.

EXAMPLE 8

The hydration reaction is run according to the same procedure as Example 3 except that the amount of water is 2 g.

EXAMPLE 9

The hydration reaction is run according to the same procedure as Example 2 except that the reaction temperature is at 60°C.

EXAMPLE 10

The hydration reaction is run according to the same procedure as Example 2 except that 10 mmol of H2O2 is added into the reaction.

EXAMPLE 11

The hydration reaction is run according to the same procedure as Example 3 except that the amount of catalyst and the reaction time are 0.05 g and 1 h, respectively.

EXAMPLE 12

The hydration reaction is run according to the same procedure as Example 11 except that the reaction temperature is at 60°C.

The results obtained in all these Examples are shown in Table 1 below.

Table 1.

Example	Catalyst nature	Catalyst amount	Amount of water	Temperature	Duration	H2O2	EG selectivity (%)	EG yield (%)
C1	TS-1	0.1 g	5g	40℃	4h	-	96.1	43.2
2	Ti-MWW	0.1 g	5g	40℃	4h	-	98.3	52.0
3	PI-Ti-MWW	0.1 g	5g	40℃	4h	-	98.1	92.4
4	HMI-Ti-MWW	0.1 g	5g	40℃	4h	-	98.1	90.7
5	Ti-MWW	0.2 g	5g	40℃	4h	-	97.6	95.4
6	Ti-MWW	0.1 g	2g	40℃	4h	-	95.3	39.1
7	PI-Ti-MWW	0.1 g	2.7g	40℃	4h	-	98.2	91.9
8	PI-Ti-MWW	0.1 g	2g	40℃	4h	-	95.2	88.3
9	Ti-MWW	0.1 g	5g	60℃	4h	-	97.5	99.5
10	Ti-MWW	0.1 g	5g	40℃	4h	10 mmol	98.2	67.1
11	PI-Ti-MWW	0.05 g	5g	40℃	1h	-	98.3	22.2
12	PI-Ti-MWW	0.05 g	5g	60℃	1h	-	98.2	76.9

CLAIMS

1. A process for the manufacture of ethylene glycol starting from ethylene oxide (EO), said process using a reaction mixture comprising EO, a Ti-MWW zeolite and water.

2. The process according to claim 1, wherein the zeolite is modified with an organic amine, preferably with piperidine or hexamethyleneimine .

3. The process according to any of the preceding claims, wherein the catalyst concentration in the reaction mixture is in the range of from 0.5 to 5 wt. %

4. The process according to any of the preceding claims, wherein the process is performed at a temperature from 20°C to 150°C.

5. The process according to any of the preceding claims, wherein the molar ratio of water to EO is in the range of from 1 to 50.

6. The process according to any of the preceding claims, wherein hydrogen peroxide in also present in the reaction mixture.

7. The process according to the preceding claim, wherein the molar ratio of hydrogen peroxide to EO is preferably in the range of from 0.01 to 10.

8. The process according to claim 6 or 7, wherein the reaction mixture also comprises a hydrogen peroxide stabilizer like a mineral acid, preferably nitric acid, and/or HEDP (1-hydroxy ethylidene-1, 1-diphosphonic acid).

9. The process according to any of the preceding claims, wherein the catalyst is a slurry catalyst or a fixed bed catalyst.

10. The process according to the preceding claim, wherein the zeolite is mixed with a binder like silica, alumina or a mixture thereof and shaped by extrusion.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2017/090500

A. CLASSIFICATION OF SUBJECT MATTER

C07C 31/20(2006.01)i; C07C 29/10(2006.01)i; C01B 39/00(2006.01)i; C01B 39/50(2006.01)i

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)

C07C; C01B

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)

CNPAT, CNKI, WPI, EPODOC, CA, STN: ethylene glycol, ethylene oxide, EO, Ti-MWW, zeolite, water, modify, catalyst, hydrogen peroxide, binder, titanosilicate, 75-21-8, 107-21-1

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	LU, Xinqing et al. "Selective synthesis of ethylene oxide through liquid-phase epoxidation of ethylene with titanosilicate/H2O2 catalytic systems" *Applied Catalysis A: General*, Vol. 515, 02 February 2016 (2016-02-02), Pages 51-59	1-10
Y	LU, Xinqing et al. "Selective synthesis of ethylene oxide through liquid-phase epoxidation of ethylene with titanosilicate/H2O2 catalytic systems" *Applied Catalysis A: General*, Vol. 515, 02 February 2016 (2016-02-02), Pages 51-59	2-10
Y	CN 101003376 A (UNIV. EAST CHINA NORMAL) 25 July 2007 (2007-07-25) description, page 2 line 4 to page 3 line 6	2-10
Y	CN 102951998 A (YUEYANG PENGCHENG TECHNOLOGY DEV. CO. LTD.) 06 March 2013 (2013-03-06) description, paragraphs [0011], [0018], [0021], [0023], [0025]-[0026], [0028]	1-10
A	CN 102219642 A (CHINA PETROLEUM & CHEM. CORP.) 19 October 2011 (2011-10-19) claims 1-7	1-10
A	US 2002010378 A1 (YUKIHIKO KAKIMOTO ET AL.) 24 January 2002 (2002-01-24) claims 1-10	1-10

☐ Further documents are listed in the continuation of Box C. ☑ 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 application or patent but published on or after the international filing date

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"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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
06 March 2018	**29 March 2018**

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2017/090500

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
CN	101003376	A	25 July 2007	CN	100460324	C	11 February 2009
CN	102951998	A	06 March 2013	CN	102951998	B	01 July 2015
CN	102219642	A	19 October 2011	CN	102219642	B	04 December 2013
US	2002010378	A1	24 January 2002	SA	1588	B1	25 November 2006
				US	6417411	B2	09 July 2002
				JP	2001316308	A	13 November 2001
				JP	3800488	B2	26 July 2006
				BE	1014247	A3	01 July 2003