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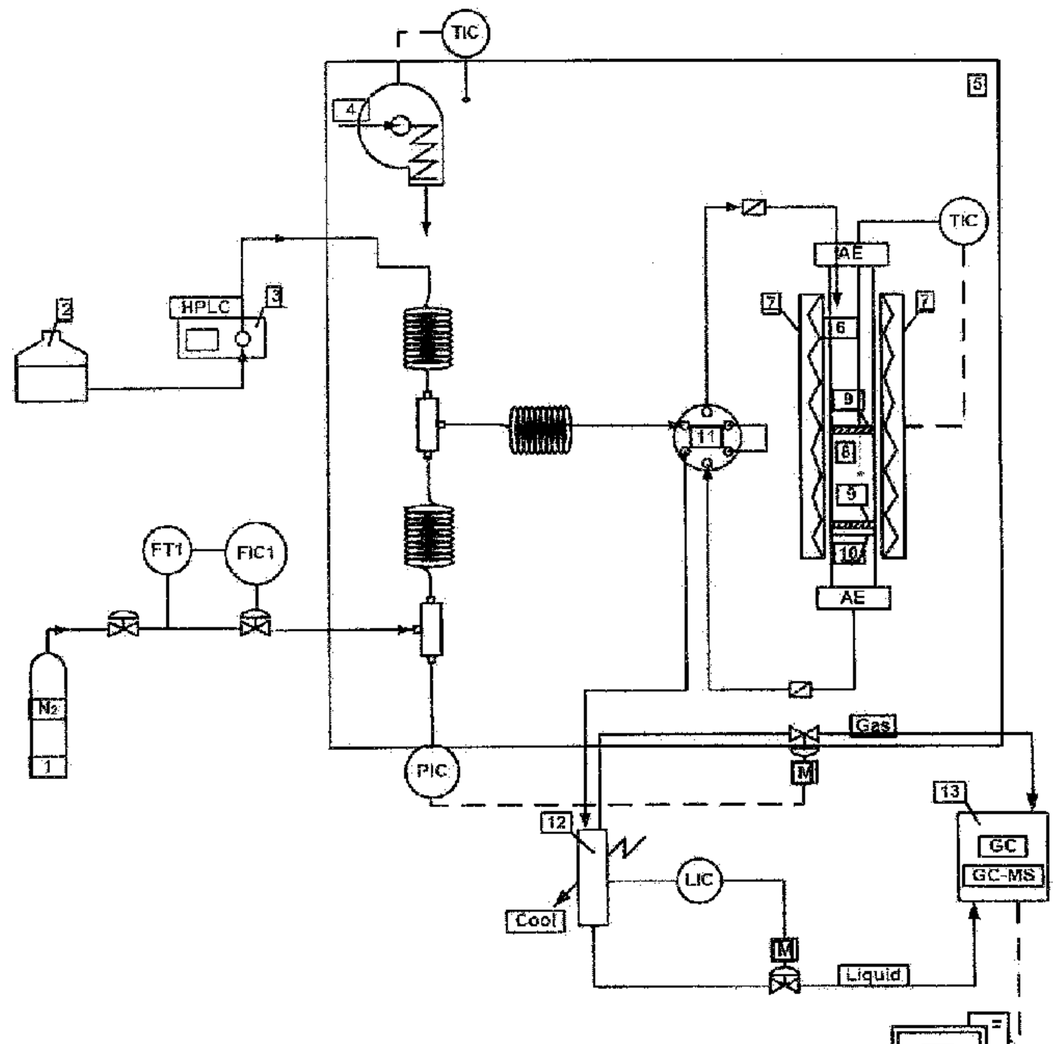
(54) ONE-STEP SYNTHESIS OF GLYCIDOL FROM GLYCEROL IN GAS-PHASE FIXED-BED CONTINUOUS FLOW REACTOR OVER ALKALI METAL PROMOTED ALUMINOSILICATE ZEOLITE CATALYST.

(57) The present invention provides a sustainable catalytic process for the production of glycidol from glycerol over alkali metal promoted aluminosilicate zeolite heterogeneous catalysts in the range of temperature 250-450 °C, glycerol concentration 1-60 wt%, gas hourly space velocity 100-2500 h^{-1} in a gas-phase fixed-bed continuous flow reactor.

FIG. 2



ONE-STEP SYNTHESIS OF GLYCIDOL FROM GLYCEROL IN GAS-PHASE FIXED-BED CONTINOUS FLOW REACTOR OVER ALKALI METAL PROMOTED ALUMINOSILICATE ZEOLITE CATALYST

SUMMARY OF THE INVENTION

The present invention relates to the use of alkali metal promoted aluminosilicate zeolite catalyst for the direct gas-phase conversion of glycerol to glycidol, as well as to a process for the production of glycidol from glycerol in a fixed-bed continuous flow reactor in the presence of such a heterogeneous catalyst. The method comprises conversion of glycerol to glycidol in the range of temperature 250-450 °C, glycerol concentration 1-60 wt%, total gas hourly space velocity 100-2500 h^{-1}, weight of catalyst 0.5-5.0 g.

BACKGROUND OF THE INVENTION

Glycerol is the major chemical for future biorefineries. According to recent studies, glycerol was detected as one of the top 12 most important bio-based chemicals in the world. Glycerol has unique substance and can be dehydrated, oxidized, reduced, halogenated, etherified, and esterified to obtain alternative commodity chemicals. The development of novel, selective chemistry to provide new applications for glycerol-derived products remains a key challenge. Therefore, new uses for glycerol need to be found.

Among various commodity chemicals proposed, there are not so many products which can be obtained in the gas-phase with high conversion and selectivity over stable catalysts. The most interesting products of the gas-phase glycerol valorization over heterogeneous catalysts are allyl alcohol, dihydroxyacetone, hydroxyacetone, acrolein, acrylic acid, lactic acid, 1,2-propanediol, 1,3-propanediol, glycerol carbonate, epichlorohydrin, and glycidol. These products are attractive for industrial commercialization due to many applications and their commercial price on the world market.

Very recently, because of the unique molecule structure, the glycidol received a special attention as a valuable product from glycerol with many potential applications as an important monomer and semi-product in the synthesis of surface-active agents, high-boiling polar solvent,

polyurethanes, polyamides, polycarbonates, polyesters, surfactants, lubricating oils, components of cosmetic preparations for skin moisturizing and purifying, hair shampoo, toothpaste, laundering detergents, disinfectants and etc. One of the most important applications of glycidol is the synthesis of analgesic and antiviral drugs, where the latter is the active compound fighting with the human immunodeficiency virus (HIV).

The computational chemistry experiments show that the reaction in gas-phase of glycerol dehydration to glycidol could pass at relatively high temperatures with dehydration mechanisms proposed for these reactions include hydride transfer, pinacol rearrangement, or substitution reactions involving the formation of cyclized products.

Nowadays, there are two the most common methods of glycidol production traditionally used. The first method is epoxidation of allyl alcohol with hydrogen peroxide, and the second is the reaction of epichlorohydrin with a caustic agent. The current problems of industrial production processes of glycidol are following: these methods consist of three stages, allyl alcohol is extremely toxic, epichlorohydrin is made from hydrocarbon feedstocks such as propylene (the raw material source is not renewable), toxic byproducts such as hydrochloric acid, expensive purification steps are necessary.

Recently, glycidol production was realized in liquid-phase from glycerol via glycerol carbonate stage, which is including of a two-step reaction: the synthesis of glycerol carbonate from glycerol and the decarboxylation of glycerol carbonate to glycidol and CO_2. The first stage of the glycerol carbonate synthesis can be realized with urea (Y. Endah, M. Kim, J. Choi, J. Jae, S. Lee, H. Lee, Catal. Today 293–294 (2017) 136–141) or dimethyl carbonate (S. Kondawar, C. Patil, C. Rode, ACS Sustain. Chem. Eng. 5 (2017) 1763–1774), in the liquid-phase over different catalysts. However, these processes have many disadvantages such as expensive catalyst, long reaction time, two-step reaction, low feedstock concentration, liquid phase reaction, batch-type reactor, high pressure, solvent, and H-donor are necessary.

In addition, the conversion of glycerol to glycidol that include the three different steps was patented by (A. Pienaar, L. Wilson, M. Stockenhuber, United States Pat. Appl. Publ. US 2013 0090497A1 (2013) 4; A. Pienaar, L. Wilson, M. Stockenhuber, United States Pat. Appl. Publ. US 20140179936A1 (2014) 5). The first step includes the dehydration of glycerol to acrolein over acidic catalyst, such as H-ZSM-5 zeolite catalyst. The second step includes the hydrogenation of acrolein to allyl alcohol over a transition metal catalysts, such as Cd, Ag or Fe

supported on a SiO_2 or Al_2O_3 support. The third step includes the epoxidation of allyl alcohol to glycidol with hydrogen peroxide over a titanium molecular sieve catalyst, such as TS-1, or Au containing catalyst. However, this method has obvious disadvantages, such as three different steps that include three different catalysts with own reaction conditions.

The production of glycidol from glycerol was studied more in liquid-phase conditions, mild temperatures, and low concentrations to avoid degradation of the highly reactive substrate. Moreover, the possibility to obtain glycidol from glycerol through the one-step reaction in the industrially more attractive continuous operation rather than in batch mode has not been investigated until now. Comparing with batch reactor the fixed-bed reactor technology is the most efficient reactor type for the synthesis. The fixed-bed continuous flow reactor was chosen by us due to the glycerol conversion and glycidol selectivity can be easily modified with parameters such as gas hourly space velocity (GHSV), temperature reaction, and catalyst weight in comparison with the batch-type reactor.

In this research, we first time investigated the one-step reaction of glycidol synthesis from glycerol in a gas-phase fixed-bed continuous flow reactor. The synthesis of the alkali metal promoted aluminosilicate zeolite catalysts was realized by the incipient wetness impregnation method with the primary focus of this study on the preparation, characterization, and performance of synthesized catalysts.

SUMMARY OF THE INVENTION

The present invention solves the problems outlined above and provides the method as defined in claim 1, as well as the catalyst defined in claim 14. Preferred embodiments of the method and the catalyst are disclosed in claims from 2 to 13 and 15 to 17 respectively, as well as in the following description.

BRIEF DESCRIPTION OF THE FIGURES

FIG. 1 shows the proposed reaction pathways for the conversion of glycerol to glycidol in the gas-phase.

FIG. 2 shows a comparison of existing routes of the gas-phase glycerol conversion into glycidol through the epoxidation reaction with the present work.

1 – N_2 gas storage tank; 2 – inlet glycerol tank; 3 – HPLC pump; 4 – convection heater, 5 – hot box; 6 – reactor; 7 – oven; 8 – packed-bed; 9 – quartz wool; 10 – steel porous plate; 11 – six port bypass valve; 12 – Peltier cooling cell; 13 – GC (Agilent GC-7890A) with FID detector and GC-MS (Shimadzu, QP2010); 14 – personal computer.

FIG. 3 shows the GC-FID chromatogram of sample after conversion of glycerol to glycidol over the 20Cs-ZSM-5 catalyst under the following reaction conditions: catalyst, 0.5 g; TOS = 3 h; $T_{reactor}$ = 350 °C; C(GL) = 10 wt%; $GHSV_{total}$ = 1250 h^{-1}.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to the use of alkali metal promoted aluminosilicate zeolite heterogeneous catalysts for the direct conversion of glycerol (GL) to glycidol (GLD) in the gas-phase fixed-bed continuous flow reactor. Preferred examples of catalysts are listed in the following: ZSM-5 (HSZ-800-840NHA, HSZ-800-890HOA, CBV 2314, CBV 3024E, CBV 5524G, CBV 8014, CBV 28014), Mordenite (CBV 10A, CBV 21A, HSZ-600-620HOA, HSZ-600-642NAA, HSZ-600-640HOA, HSZ-600-660HOA, HSZ-600-690HOA), USY (HSZ-300-320NAA, HSZ-300-320HOA, HSZ-300-331HSA, HSZ-300-330HUA, HSZ-300-341NHA, HSZ-300-350HUA, HSZ-300-360HUA, HSZ-300-385HUA, HSZ-300-390HUA), Zeolite L (HSZ-500-500KOA), Ferrierite (HSZ-700-720KOA, CP914C), Zeolite Beta (HSZ-900-931HOA, HSZ-900-940HOA, HSZ-900-980HOA, CP814E, CP814C, CP811C-300), Zeolite Y (CBV 100, CBV 300, CBV 400, CBV 500, CBV 600, CBV 712, CBV 720, CBV 760, CBV 780, CBV 901), Cs oxides, $CsNO_3$, Cs_2SO_4, CsF, CsCl, CsBr, CsI, Cs_3PO_4, Cs_2CO_3, $Cs_2C_2O_4$, CH_3CO_2Cs (with varying Cs loading, preferably from 1 to 60), Li oxides, $LiNO_3$, Li_2SO_4, LiF, LiCl, LiBr, LiI, Li_3PO_4, Li_2CO_3, $Li_2C_2O_4$, CH_3CO_2Li (with varying Li loading, preferably from 1 to 60), Na oxides, $NaNO_3$, Na_2SO_4, NaF, NaCl, NaBr, NaI, Na_3PO_4, Na_2CO_3, $Na_2C_2O_4$, CH_3CO_2Na (with varying Na loading, preferably from 1 to 60), K oxides, KNO_3, K_2SO_4, KF, KCl, KBr, KI, K_3PO_4, K_2CO_3, $K_2C_2O_4$, CH_3CO_2K (with varying K loading, preferably from 1 to 60), Rb oxides,

$RbNO_3$, Rb_2SO_4, RbF, RbCl, RbBr, RbI, Rb_3PO_4, Rb_2CO_3, $Rb_2C_2O_4$, CH_3CO_2Rb (with varying Rb loading, preferably from 1 to 60).

Preferred catalysts are based on the ZSM-5 aluminosilicate zeolite promoted with $CsNO_3$.

The suitable amount of alkali metal in the catalysts of the present invention is in the range of from 1 to 60 weight percent relative to the zeolite support. The following examples merely illustrate the invention. It is to be understood that the preferred embodiments described for the catalyst as such of course also are applicable to the use of the catalyst in the process of the present invention.

Examples of suitable alkali metal promoted aluminosilicate zeolite catalysts are xCs-zeolite, xLi-zeolite, xNa-zeolite, xK-zeolite, xRb-zeolite, preferably xCs-zeolite, wherein the alkali metal are supported on a ZSM-5 (HSZ-800-840NHA, HSZ-800-890HOA, CBV 2314, CBV 3024E, CBV 5524G, CBV 8014, CBV 28014), Mordenite (CBV 10A, CBV 21A, HSZ-600-620HOA, HSZ-600-642NAA, HSZ-600-640HOA, HSZ-600-660HOA, HSZ-600-690HOA), USY (HSZ-300-320NAA, HSZ-300-320HOA, HSZ-300-331HSA, HSZ-300-330HUA, HSZ-300-341NHA, HSZ-300-350HUA, HSZ-300-360HUA, HSZ-300-385HUA, HSZ-300-390HUA), Zeolite L (HSZ-500-500KOA), Ferrierite (HSZ-700-720KOA, CP914C), Zeolite Beta (HSZ-900-931HOA, HSZ-900-940HOA, HSZ-900-980HOA, CP814E, CP814C, CP811C-300), Zeolite Y (CBV 100, CBV 300, CBV 400, CBV 500, CBV 600, CBV 712, CBV 720, CBV 760, CBV 780, CBV 901), wherein most preferably ZSM-5. The alkali metals to be employed in accordance with the present invention are preferably selected among oxide, nitrate, sulfate, chloride, phosphate, carbonate, iodide, bromide, fluoride, oxalate, acetic salts, wherein most preferably nitrate salts.

The catalysts in accordance with the present invention preferably are aluminosilicate zeolite ZSM-5 and cesium alkali metal supported on this material. The suitable amount of alkali metal in the zeolite support of the present invention is in the range of from 1 to 60 weight percent relative to the support.

The catalysts disclosed herein, in particular the xCs-zeolite, xLi-zeolite, xNa-zeolite, xK-zeolite, xRb-zeolite catalytic system disclosed herein has particularly shown to efficiently gas-phase glycerol conversion in a fixed-bed reactor. Without being bound to the following explanation, it may be that the superior and unexpected activity is attributed to the presence of Lewis and Brönsted acid-base sites, and synergetic interaction between Cs species and zeolite

support. The suitable balance between acidity-basicity of the catalyst samples are the key parameter to the high selectivity for the desired glycidol production. In any case, the xCs-ZSM-5 zeolite catalytic system disclosed here shows first time high activity and selectivity of GLD from GL in a gas-phase fixed-bed continuous flow reactor - higher than other catalysts tested or reported in the literature for the gas-phase conversion of GL to GLD.

In order to demonstrate the superiority of the present invention, these following catalysts have been evaluated in relation with the catalytic conversion of GL to GLD, including ZSM-5 (HSZ-800-840NHA, HSZ-800-890HOA, CBV 2314, CBV 3024E, CBV 5524G, CBV 8014, CBV 28014), Mordenite (CBV 10A, CBV 21A, HSZ-600-620HOA, HSZ-600-642NAA, HSZ-600-640HOA, HSZ-600-660HOA, HSZ-600-690HOA), USY (HSZ-300-320NAA, HSZ-300-320HOA, HSZ-300-331HSA, HSZ-300-330HUA, HSZ-300-341NHA, HSZ-300-350HUA, HSZ-300-360HUA, HSZ-300-385HUA, HSZ-300-390HUA), Zeolite L (HSZ-500-500KOA), Ferrierite (HSZ-700-720KOA, CP914C), Zeolite Beta (HSZ-900-931HOA, HSZ-900-940HOA, HSZ-900-980HOA, CP814E, CP814C, CP811C-300), Zeolite Y (CBV 100, CBV 300, CBV 400, CBV 500, CBV 600, CBV 712, CBV 720, CBV 760, CBV 780, CBV 901), Cs oxides, $CsNO_3$, Cs_2SO_4, CsF, CsCl, CsBr, CsI, Cs_3PO_4, Cs_2CO_3, $Cs_2C_2O_4$, CH_3CO_2Cs (with varying Cs loading, preferably from 1 to 60), Li oxides, $LiNO_3$, Li_2SO_4, LiF, LiCl, LiBr, LiI, Li_3PO_4, Li_2CO_3, $Li_2C_2O_4$, CH_3CO_2Li (with varying Li loading, preferably from 1 to 60), Na oxides, $NaNO_3$, Na_2SO_4, NaF, NaCl, NaBr, NaI, Na_3PO_4, Na_2CO_3, $Na_2C_2O_4$, CH_3CO_2Na (with varying Na loading, preferably from 1 to 60), K oxides, KNO_3, K_2SO_4, KF, KCl, KBr, KI, K_3PO_4, K_2CO_3, $K_2C_2O_4$, CH_3CO_2K (with varying K loading, preferably from 1 to 60), Rb oxides, $RbNO_3$, Rb_2SO_4, RbF, RbCl, RbBr, RbI, Rb_3PO_4, Rb_2CO_3, $Rb_2C_2O_4$, CH_3CO_2Rb (with varying Rb loading, preferably from 1 to 60). The respective results, some of which are discussed further in relation with experimental data shown below, prove that the catalysts in accordance with the present invention enable the preparation of the desired target molecule in a highly effective manner, thereby overcoming the drawbacks associated with the prior art and solving the problems outlined above.

Accordingly the process in accordance with the present invention comprises the step of converting a starting material, selected GL water solution, preferably obtained from renewable resources (bio-based) to GLD in the presence of a heterogeneous catalysts as defined above, preferably selected among catalysts based on zeolite, preferably selected among ZSM-5 (HSZ-

800-840NHA, HSZ-800-890HOA, CBV 2314, CBV 3024E, CBV 5524G, CBV 8014, CBV 28014), Mordenite (CBV 10A, CBV 21A, HSZ-600-620HOA, HSZ-600-642NAA, HSZ-600-640HOA, HSZ-600-660HOA, HSZ-600-690HOA), USY (HSZ-300-320NAA, HSZ-300-320HOA, HSZ-300-331HSA, HSZ-300-330HUA, HSZ-300-341NHA, HSZ-300-350HUA, HSZ-300-360HUA, HSZ-300-385HUA, HSZ-300-390HUA), Zeolite L (HSZ-500-500KOA), Ferrierite (HSZ-700-720KOA, CP914C), Zeolite Beta (HSZ-900-931HOA, HSZ-900-940HOA, HSZ-900-980HOA, CP814E, CP814C, CP811C-300), Zeolite Y (CBV 100, CBV 300, CBV 400, CBV 500, CBV 600, CBV 712, CBV 720, CBV 760, CBV 780, CBV 901), preferably ZSM-5, as well as alkali metals, wherein the alkali metals are supported on a ZSM-5, preferably selected among those exemplified above. As for the catalyst, as such the alkali metals to be employed in accordance with the present invention are preferably selected among Li, Na, K, Rb, Cs, most preferably Cs. These alkali metals preferably selected among oxide, nitrate, sulfate, chloride, phosphate, carbonate, iodide, bromide, fluoride, oxalate, acetate salts, wherein preferably nitrate salts.

The starting materials to be converted in accordance with the present invention typically are provided in a polar solvent, preferably water. It has been found that the concentration of the starting material in the polar solvent preferably is at least 1 wt% and not more than 60 wt%, preferably 10 to 35 wt%. It has been found that the amount of catalyst in the gas-phase reaction in fixed-bed continuous flow reactor is not less than 0.5 g and not higher than 5.0 g.

The gas hourly space velocity is in the range of from 100 to 2500 h^{-1}, preferably from 300 to 2000 h^{-1} and more preferably from 500 to 1500 h^{-1}, and most preferably 1000-1250 h^{-1}. A preferred combination of reaction conditions is a temperature of from 330 to 360 °C and a gas hourly space velocity of from 1000 to 1250 h^{-1}. Preferably, the reaction is carried out with a carrier gas, and nitrogen gas is a preferred example of a suitable carrier gas, due to its abundance and low cost.

The process disclosed here typically is carried out at a temperature of from 250 to 450 °C, preferably from 300 to 350 °C, more preferably from 330 to 360 °C, such as 350 °C. The reaction may be carried out in any suitable reactors known to the skilled person, but stainless steel reactors (fixed-bed continuous flow reactor) are in particular suitable.

It is to be understood, that the various process parameters, such as starting material concentration, gas-hourly space velocity, catalyst amount, temperature, while being disclosed

individually, are considered in the context of the present invention in combination, such as a process employing water as solvent, a starting material concentration of from 1 to 60 wt%, a catalyst amount of from 0.5 to 5.0 g, a reaction temperature of from 250 to 450 °C, and a the gas hourly space velocity of from 100 to 2500 h^{-1}. However, all other combinations possible from the ranges and preferred embodiments are also comprised by and disclosed in this invention.

In the examples described herein, the catalytic conversion of glycerol was performed using a stainless steel fixed-bed continuous flow reactor under the standard operation conditions. The novel process of the present invention was carried out at a temperature greater than 250 °C, most preferably between 250 and 450 °C, especially between 330 and 360°C. The reactions were carried out under atmospheric pressure. In general, the reaction should be conducted under conditions where the gas hourly space velocity of the feedstock solution over the catalyst is appropriate to generate the desired products. Preferably, the gas hourly space velocity is in the range of between 100 and 2500 h^{-1}, typically 300-1500 h^{-1}, more preferably 500-1000 h^{-1}, most preferably 1000-1250 h^{-1}.

EXAMPLES

The following examples are included to further illustrate various embodiments of the presently disclosed subject matter. However, those of ordinary skill in the art should, in light of the present disclosure, appreciate that many changes can be made in specific embodiments which are disclosed and still obtain like or similar results without departing from the spirit and scope of the presently disclosed subject matter.

EXAMPLE 1

Materials used

In the next examples, the following starting materials were used: ZSM-5 (HSZ-800-840NHA, HSZ-800-890HOA, CBV 2314, CBV 3024E, CBV 5524G, CBV 8014, CBV 28014), $CsNO_3$ (Sigma-Aldrich, 99%), glycerol (Sigma-Aldrich, 99%), nitrogen (5.0, Messer, Bad Soden am Taunus, Germany), NH_3 (10 vol% in He, Linde, Pullach, Germany), helium (5.0, Messer, Bad Soden am Taunus, Germany) and carbon dioxide (10 vol% CO_2 in He, Linde, Pullach, Germany),

glycidol (Sigma-Aldrich, 96%), acrolein (Fluka, >95%), allyl alcohol (Sigma-Aldrich, >99%), hydroxyacetone (Alfa Aesar, 95%), 2-methoxy-1,3-dioxalane (Sigma-Aldrich, >99%), glycerol formal (Sigma-Aldrich, 98%), acetaldehyde (Sigma-Aldrich, >99.5%), propionaldehyde (Sigma-Aldrich, 97%), acetic acid (Sigma-Aldrich, >99.7%), acetone (Sigma-Aldrich, >99.5%), propionic acid (Sigma-Aldrich, >99.5%), acrylic acid (Sigma-Aldrich, 99%), 1,2-propanediol (Sigma-Aldrich, >99%), n-propanol (Sigma-Aldrich, 99.5%), formaldehyde (Sigma-Aldrich, 37wt% in H_2O), methanol (Sigma-Aldrich, >99.9%).

EXAMPLE 2

Catalysts preparation

The preparation of the alkali metal promoted aluminosilicate zeolite catalysts has involved the impregnation of zeolite support using the incipient wetness impregnation method with solutions 0.01 M of alkali metal. The zeolite support were calcined at 550 °C in air for 6 h to convert the powder from the ammonium form to its protonated form and/or to completely remove any organic residues from the protonated form. The alkali metal solution was added to the corresponding zeolite with vigorous stirring and 80 °C. Stirring continued until suspension turned into a slurry. Then samples were dried overnight at 110 °C and calcined at 550 °C for 6 hours.

EXAMPLE 3

The Fig.1 presents a possible general reaction pathway for glycerol conversion by consecutive and/or parallel dehydration-hydrogenation-oxidation-epoxidation reactions with the participation of Lewis and Brönsted acid-base sites on the alkali metal promoted zeolite catalyst. It is well known that hydroxyacetone and acrolein are both products of the dehydration of glycerol. We speculate that glycidol could be obtained from allyl alcohol through the epoxidation reaction, where the allyl alcohol can be obtained from acrolein by a transfer hydrogenation reaction. Using alkali metal promoted aluminosilicate zeolite catalyst, we have succeeded in producing of glycidol as the main product. At the same time, by-products were obtained from glycerol feed, such as allyl alcohol, hydroxyacetone, acrolein, acetaldehyde, acetic acid, 1,2-propanediol, propionaldehyde, propionic acid, and acrylic acid.

EXAMPLE 4

Catalytic evaluation

The gas-phase conversion of GL into GLD (Fig. 2) was studied in an automated laboratory fixed-bed microactivity reactor (Microactivity-Reference, PID Eng&Tech). 0.5 g of the alkali metal promoted aluminosilicate zeolite catalyst was placed in a packed bed tubular reactor and stabilized with glass wool on both sides. The glycerol of 1-60 wt% aqueous solution was kept at room temperature in a reservoir tank (3) outside of the hot box. It was injected into the hot box with a 307 HPLC Piston Pump (4) (Gilson Inc.). The N_2 gas was introduced into the hot box (6) with mass flow controllers (FT1). The glycerol aqueous solution was entered to the hot box (6) was vaporized, since the inside temperature was held at 140 °C, with the help of an electric convection heater (5), controlled by the temperature controller, TIC. After it was mixed of the glycerol solution vapour and was introduced N_2 gas. The inlet stream was then passed through a six-port VICI reactor standard bypass valve (12) and was either introduced into the reactor (7) or sent out of the reactor. The reactor was a stainless steel tube (9 mm internal diameter, 305 mm long). The catalyst was packed inside of the tube (9) and insulated with a 15 mm layer of glass wool at the top and bottom (10). The temperature of the packed-bed was measured with a thermocouple with the TIC controller. After leaving the reactor tube, the outlet stream was conducted through the six-port bypass valve (12) and into the Peltier cell (13). The product was cooled down inside the internal storage. The liquid level in the storage was controlled with a level controller (LIC) and the excess product was sent into absorber placed below the reactor.

The collected liquid samples were then analyzed by gas chromatography GC (Agilent GC-7890A) with measurement repeatability of the relative standard deviation (RSD) $\leq$ 5% equipped with FID detector. Hydrogen used as carrier gas with a flow rate of 1 mL/min. The capillary column was 30m × 0.25mm × 0.25μm DB-WAX Ultra Inert. To achieve effective product separation, the column was held at 40 °C for 4 min before the temperature was ramped up to 200 °C at a rate of 12 °C/min and remained there for 10 min. The split ratio was 1:150. All products were quantified via an external calibration method verified by a gas chromatography-mass spectrometry system (Shimadzu, GC/MS-QP2010) with the capillary column 30m x 0.25mm x 0.5um Zebron ZB-WAX-Plus.

Calibration curves were measured in the 0.1-10 wt% range by using chemicals mentioned above in the chemical used paragraph. The conversion of glycerol, X_{GL}, and the selectivity to the product *i,* S*i*, calculated using the equations below, where *n* refers to the moles of compound and in/out to the reactor inlet/outlet.

$$X_{GL}\,(\mathrm{mol\%}) = \frac{\left(n_{GL}^{in} - n_{GL}^{out}\right)}{n_{GL}^{in}} \times 100\,;$$

$$S_i\,(\mathrm{mol\%}) = \frac{n_i}{n_{GL}^{in} - n_{GL}^{out}} \times \frac{Z_i}{Z_{GL}} \times 100\,;$$

$$Y_i\,(\mathrm{mol\%}) = \frac{n_i}{n_{GL}^{in}} \times \frac{Z_i}{Z_{GL}} \times 100\,;$$

where n_{GL}^{in} and n_{GL}^{out} are the input and output flows of glycerol (mol/min), n_i is the flow of the products *i* (mol/min), Z_{GL} = 3 (the number of carbon atoms in the GL molecule), and Z_i represents the number of carbon atoms in the products. The values in this article are in mole percent. The mass balance was calculated for each experiment and was usually above 92%, where the difference in mass balance was in the range of the experimental error. The studied conversion and selectivity figures were calculated by the values of three measurements.

EXAMPLE 5

GC-FID traces for a typical run over the 20wt%Cs-ZSM-5 catalyst shows on the Fig. 3 the formation of GLD, hydroxyacetone, allyl alcohol, 1,2-propanediol, acrolein, acetaldehyde, acetic acid, and propionic acid liquid products formation over the 20wt%Cs-ZSM-5 catalyst with $GHSV_{total}$ = 1250 h^{-1}. These products approximately covered of 96% from the total mass.

EXAMPLE 6

Product distribution over cesium promoted ZSM-5 zeolite catalysts in the gas-phase reaction of GL to GLD

The conversion of GL to GLD has been performed in the same conditions as those described in the example above (Catalyst evaluation paragraph). The results obtained with over of the catalysts of formula xCs-ZSM-5 are given in Table 1 below:

Table 1. Product distribution data over cesium promoted ZSM-5 zeolite catalysts in the gas-phase glycerol conversion to glycidol

Catalyst	Glycidol selectivity (mol%)	Hydroxyacetone selectivity (mol%)	1,2-Propanediol selectivity (mol%)	Acrolein selectivity (mol%)	Allyl alcohol selectivity (mol%)	Others (mol%)	Time-on-stream (h)
10Cs-ZSM-5	42.9	38.7	3.8	5.6	1.5	7.5	27
20Cs-ZSM-5	64.3	28.1	2.8	0.5	2.7	1.6	27
40Cs-ZSM-5	56.2	32.1	5.2	1.8	4.7	0	27

EXAMPLE 7

Catalytic conversion of GL to GLD over cesium promoted ZSM-5 zeolite catalysts in a fixed-bed continuous flow reactor

These results show the glycidol yield and glycerol conversion in the same conditions as those of example 6. The results are tabulated in Table 2 below:

Table 2. Gas-phase glycerol conversion and glycidol yield over cesium promoted ZSM-5 zeolite catalysts in a fixed-bed continuous flow reactor

Catalyst	Glycidol yield (mol%)	Glycerol conversion (mol%)	Time-on-stream (h)
10Cs-ZSM-5	12.5	32.9	3
20Cs-ZSM-5	40.4	86.3	3
40Cs-ZSM-5	4.7	21.8	2

CLAIMS

1. Process for the production of glycidol (GLD) comprising the steps:
   (a) feeding a starting material over a heterogeneous catalyst into a fixed-bed continuous flow reactor,
   (b) heating said mixture at a temperature ranging from 250 to 450 °C to obtain glycidol,
   (c) flowing N_2 as a carrier gas and glycerol (GL) as a feed with total gas hourly space velocity 100-2500 h^{-1},
   (d) and collecting the GLD product,
   wherein the starting material is GL solution, and wherein the catalyst is a heterogeneous catalyst.

2. The process as claimed in claim 1, wherein the catalyst comprises at least one alkali metal compound supported on aluminosilicate zeolite.

3. The process as claimed in claim 1 or 2, wherein the heterogeneous catalyst comprises alkali metals in an amount of 1 to 60 wt%.

4. The process as claimed in claim 2 or 3, wherein the alkali metals are selected from lithium (Li), sodium (Na), potassium (K), rubidium (Rb), and cesium (Cs).
   The process as claimed in any one of claims 2-4, wherein the zeolite is selected from the group consisting of ZSM-5 (HSZ-800-840NHA, HSZ-800-890HOA, CBV 2314, CBV 3024E, CBV 5524G, CBV 8014, CBV 28014), Mordenite (CBV 10A, CBV 21A, HSZ-600-620HOA, HSZ-600-642NAA, HSZ-600-640HOA, HSZ-600-660HOA, HSZ-600-690HOA), USY (HSZ-300-320NAA, HSZ-300-320HOA, HSZ-300-331HSA, HSZ-300-330HUA, HSZ-300-341NHA, HSZ-300-350HUA, HSZ-300-360HUA, HSZ-300-385HUA, HSZ-300-390HUA), Zeolite L (HSZ-500-500KOA), Ferrierite (HSZ-700-720KOA, CP914C), Zeolite Beta (HSZ-900-931HOA, HSZ-900-940HOA, HSZ-900-980HOA, CP814E, CP814C, CP811C-300), and Zeolite Y (CBV 100, CBV 300, CBV 400, CBV 500, CBV 600, CBV 712, CBV 720, CBV 760, CBV 780, CBV 901), preferably ZSM-5.

5. The process as claimed in any one of claims 2-4, wherein the alkali metal compounds are selected from the group consisting of Cs oxides, $CsNO_3$, Cs_2SO_4, CsF, CsCl, CsBr, CsI, Cs_3PO_4, Cs_2CO_3, $Cs_2C_2O_4$, CH_3CO_2Cs (with varying Cs loading, preferably from 1 to 60), Li oxides, $LiNO_3$, Li_2SO_4, LiF, LiCl, LiBr, LiI, Li_3PO_4, Li_2CO_3, $Li_2C_2O_4$, CH_3CO_2Li (with varying Li loading, preferably from 1 to 60), Na oxides, $NaNO_3$, Na_2SO_4, NaF, NaCl, NaBr, NaI, Na_3PO_4, Na_2CO_3, $Na_2C_2O_4$, CH_3CO_2Na (with varying Na loading, preferably from 1 to 60), K oxides, KNO_3, K_2SO_4, KF, KCl, KBr, KI, K_3PO_4, K_2CO_3, $K_2C_2O_4$, CH_3CO_2K (with varying K loading, preferably from 1 to 60), Rb oxides, $RbNO_3$, Rb_2SO_4, RbF, RbCl, RbBr, RbI, Rb_3PO_4, Rb_2CO_3, $Rb_2C_2O_4$, CH_3CO_2Rb (with varying Rb loading, preferably from 1 to 60).

6. The process according to any one of the preceding claims, wherein the catalyst is selected from the group consisting of xLi-zeolite, xNa-zeolite, xK-zeolite, xRb-zeolite, and xCs-zeolite, preferably xCs-ZSM-5 aluminosilicate zeolite.

7. The process as claimed in at least one of the preceding claims, wherein the amount of catalysts ranges from 0.5 to 5 g.

8. The process as claimed in any of the preceding claims, wherein the concentration of GL is in the range from 1 to 60 wt%.

9. The process according to any one of the preceding claims, wherein the temperature is from 250 °C to 450 °C.

10. The process according to any one of the preceding claims, wherein the gas hourly space velocity is from 100 to 2500 h^{-1}.

11. Catalyst for the production of GLD from GL, wherein the catalyst is a heterogeneous catalyst, comprising at least one alkali metal compound supported on aluminosilicate zeolite.

12. The catalyst as claimed in claim 11, wherein the heterogeneous catalyst comprises alkali metals in an amount of 1 to 60 wt%.

13. The catalyst as claimed in claim 11 or 12, wherein the alkali metals are selected from lithium (Li), sodium (Na), potassium (K), rubidium (Rb), and cesium (Cs).

14. The catalyst as claimed in any one of claims 11-13, wherein the zeolite is selected from the group consisting of ZSM-5 (HSZ-800-840NHA, HSZ-800-890HOA, CBV 2314, CBV 3024E, CBV 5524G, CBV 8014, CBV 28014), Mordenite (CBV 10A, CBV 21A, HSZ-600-620HOA, HSZ-600-642NAA, HSZ-600-640HOA, HSZ-600-660HOA, HSZ-600-690HOA), USY (HSZ-300-320NAA, HSZ-300-320HOA, HSZ-300-331HSA, HSZ-300-330HUA, HSZ-300-341NHA, HSZ-300-350HUA, HSZ-300-360HUA, HSZ-300-385HUA, HSZ-300-390HUA), Zeolite L (HSZ-500-500KOA), Ferrierite (HSZ-700-720KOA, CP914C), Zeolite Beta (HSZ-900-931HOA, HSZ-900-940HOA, HSZ-900-980HOA, CP814E, CP814C, CP811C-300), and Zeolite Y (CBV 100, CBV 300, CBV 400, CBV 500, CBV 600, CBV 712, CBV 720, CBV 760, CBV 780, CBV 901), preferably ZSM-5.

15. The catalyst as claimed in any one of claims 11-14, wherein the alkali metal compounds are selected from the group consisting of Cs oxides, $CsNO_3$, Cs_2SO_4, CsF, CsCl, CsBr, CsI, Cs_3PO_4, Cs_2CO_3, $Cs_2C_2O_4$, CH_3CO_2Cs (with varying Cs loading, preferably from 1 to 60), Li oxides, $LiNO_3$, Li_2SO_4, LiF, LiCl, LiBr, LiI, Li_3PO_4, Li_2CO_3, $Li_2C_2O_4$, CH_3CO_2Li (with varying Li loading, preferably from 1 to 60), Na oxides, $NaNO_3$, Na_2SO_4, NaF, NaCl, NaBr, NaI, Na_3PO_4, Na_2CO_3, $Na_2C_2O_4$, CH_3CO_2Na (with varying Na loading, preferably from 1 to 60), K oxides, KNO_3, K_2SO_4, KF, KCl, KBr, KI, K_3PO_4, K_2CO_3, $K_2C_2O_4$, CH_3CO_2K (with varying K loading, preferably from 1 to 60), Rb oxides, $RbNO_3$, Rb_2SO_4, RbF, RbCl, RbBr, RbI, Rb_3PO_4, Rb_2CO_3, $Rb_2C_2O_4$, CH_3CO_2Rb (with varying Rb loading, preferably from 1 to 60).

16. The catalyst as claimed in any one of the preceding claims, wherein the catalyst is selected from the group consisting of xLi-zeolite, xNa-zeolite, xK-zeolite, xRb-zeolite, and xCs-zeolite, preferably xCs-ZSM-5 aluminosilicate zeolite.

17. The catalyst as claimed in any one of claims 11-16, showing in the production of GLD from GL in the gas-phase fixed-bed continuous flow reactor conversion of the GL, of more than 86 mol% and a yield of GLD of above 40 mol%.

Ansprüche

1. Verfahren zur Herstellung von Glycidol (GLD), umfassend die Schritte:
   (a) Zuführen eines Startmaterials über einen heterogenen Katalysator in einen Festbett-Durchlaufreaktor,
   (b) Erhitzen der genannten Mischung bei einer Temperatur im Bereich von 250 bis 450 °C, um Glycidol zu erhalten,
   (c) Strömen von N_2 als Trägergas und Glycerol (GL) als Zufuhrmaterial mit einer stündlichen Gesamtgasraumgeschwindigkeit von 100-2500 h^{-1},
   (d) und Sammeln des GLD Produkts,
   wobei das Startmaterial eine GL-Lösung ist und wobei der Katalysator ein heterogener Katalysator ist.

2. Verfahren nach Anspruch 1, wobei der Katalysator wenigstens eine auf einem Alumosilikat-Zeolith fixierte Alkalimetallverbindung umfasst.

3. Verfahren nach Anspruch 1 oder 2, wobei der heterogene Katalysator Alkalimetalle in einer Menge von 1 bis 60 Gew.-% umfasst.

4. Verfahren nach Anspruch 2 oder 3, wobei die Alkalimetalle aus Lithium (Li), Natrium (Na), Kalium (K), Rubidium (Rb) und Caesium (Cs) ausgewählt sind.

5. Verfahren nach einem der Ansprüche 2-4, wobei der Zeolith ausgewählt ist aus der Gruppe bestehend aus ZSM-5 (HSZ-800-840NHA, HSZ-800-890HOA, CBV 2314, CBV 3024E, CBV 5524G, CBV 8014, CBV 28014), Mordenit (CBV 10A, CBV 21A, HSZ-600-620HOA, HSZ-600-642NAA, HSZ-600-640HOA, HSZ-600-660HOA, HSZ-600-690HOA), USY (HSZ-300-320NAA, HSZ-300-320HOA, HSZ-300-331HSA, HSZ-300-330HUA, HSZ-300-341NHA, HSZ-300-350HUA, HSZ-300-360HUA, HSZ-300-385HUA, HSZ-300-390HUA), Zeolith L (HSZ-500-500KOA), Ferrierit (HSZ-700-720KOA, CP914C), Zeolith Beta (HSZ-900-931HOA, HSZ-900-940HOA, HSZ-900-980HOA, CP814E, CP814C, CP811C-300) und Zeolith Y (CBV 100, CBV 300, CBV 400, CBV 500, CBV 600, CBV 712, CBV 720, CBV 760, CBV 780, CBV 901), bevorzugt ZSM-5.

6. Verfahren nach einem der Ansprüche 2-4, wobei die Alkalimetallverbindungen ausgewählt sind aus der Gruppe bestehend aus Cs-Oxiden, $CsNO_3$, Cs_2SO_4, CsF, CsCl, CsBr, CsI, Cs_3PO_4, Cs_2CO_3, $Cs_2C_2O_4$, CH_3CO_2Cs (mit variierender Cs-Beladung, bevorzugt von 1 bis 60), Li-Oxiden, $LiNO_3$, Li_2SO_4, LiF, LiCl, LiBr, LiI, Li_3PO_4, Li_2CO_3, $Li_2C_2O_4$, CH_3CO_2Li (mit variierender Li-Beladung, bevorzugt von 1 bis 60), Na-Oxiden, $NaNO_3$, Na_2SO_4, NaF, NaCl, NaBr, NaI, Na_3PO_4, Na_2CO_3, $Na_2C_2O_4$, CH_3CO_2Na (mit variierender Na-Beladung, bevorzugt von 1 bis 60), K-Oxiden, KNO_3, K_2SO_4, KF, KCl, KBr, KI, K_3PO_4, K_2CO_3, $K_2C_2O_4$, CH_3CO_2K (mit variierender K-Beladung, bevorzugt von 1 bis 60), Rb-Oxiden, $RbNO_3$, Rb_2SO_4, RbF, RbCl, RbBr, RbI, Rb_3PO_4, Rb_2CO_3, $Rb_2C_2O_4$, CH_3CO_2Rb (mit variierender Rb-Beladung, bevorzugt von 1 bis 60).

7. Verfahren nach einem der vorhergehenden Ansprüche, wobei der Katalysator ausgewählt ist aus der Gruppe bestehend aus xLi-Zeolith, xNa-Zeolith, xK-Zeolith, xRb-Zeolith und xCs-Zeolith, bevorzugt xCs-ZSM-5 Alumosilikatzeolith.

8. Verfahren nach mindestens einem der vorhergehenden Ansprüche, wobei die Menge des Katalysators im Bereich von 0.5 bis 5 g liegt.

9. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Konzentration an GL im Bereich von 1 bis 60 Gew.-% liegt.

10. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Temperatur von 250 °C bis 450 °C reicht.

11. Verfahren nach einem der vorhergehenden Ansprüche, wobei die stündliche Gasraumgeschwindigkeit von 100 bis 2500 h^{-1} reicht.

12. Katalysator für die Herstellung von GLD aus GL, wobei der Katalysator ein heterogener Katalysator ist, der wenigstens eine auf einem Alumosilikatzeolith fixierte Alkalimetallverbindung umfasst.

13. Katalysator nach Anspruch 12, wobei der heterogene Katalysator Alkalimetalle in einer Menge von 1 bis 60 Gew.-% umfasst.

14. Katalysator nach Anspruch 12 oder 13, wobei die Alkalimetalle aus Lithium (Li), Natrium (Na), Kalium (K), Rubidium (Rb) und Caesium (Cs) ausgewählt sind

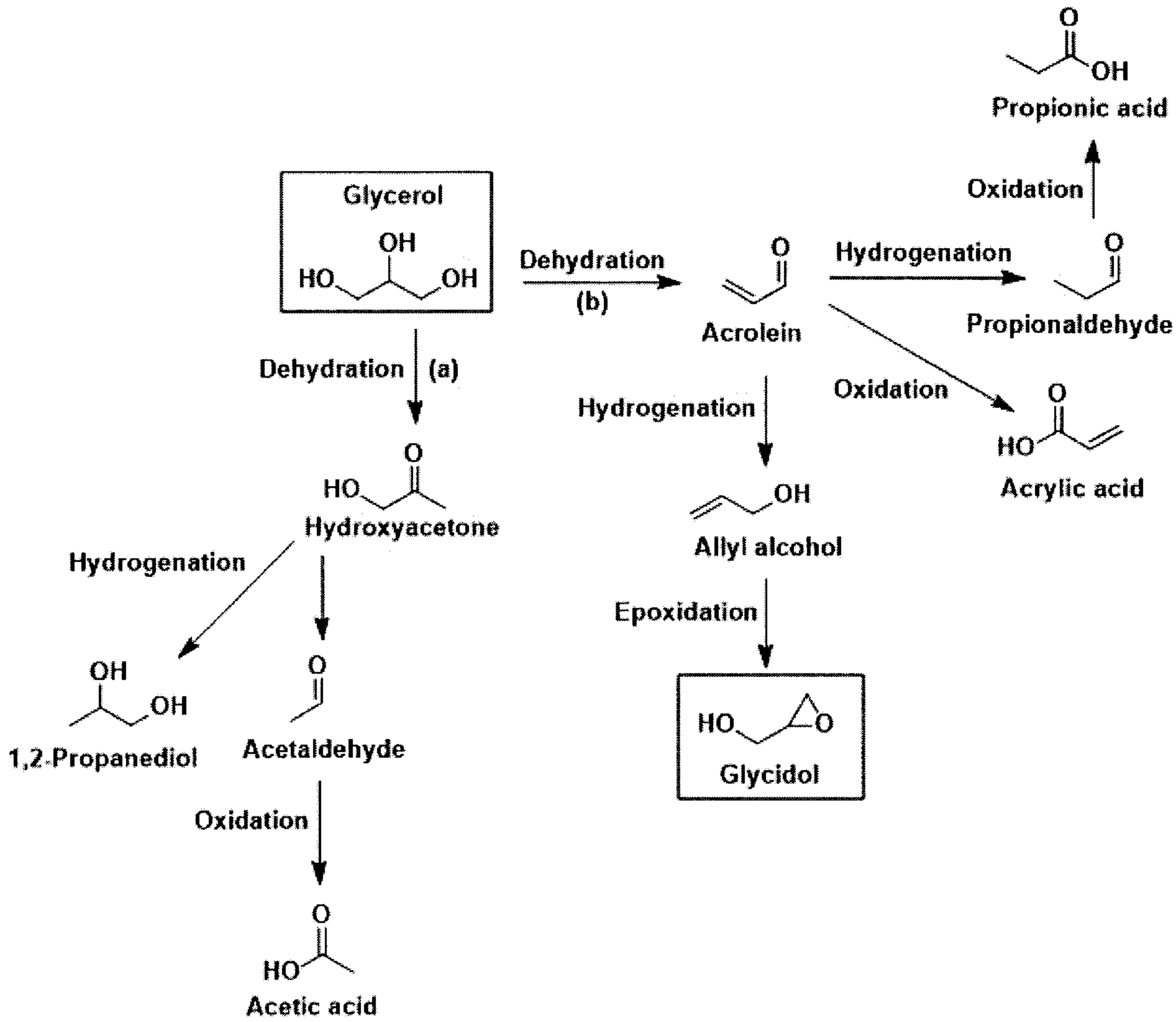
15. Katalysator nach einem der Ansprüche 12-14, wobei der Zeolith ausgewählt ist aus der Gruppe bestehend aus ZSM-5 (HSZ-800-840NHA, HSZ-800-890HOA, CBV 2314, CBV 3024E, CBV 5524G, CBV 8014, CBV 28014), Mordenit (CBV 10A, CBV 21A, HSZ-600-620HOA, HSZ-600-642NAA, HSZ-600-640HOA, HSZ-600-660HOA, HSZ-600-690HOA), USY (HSZ-300-320NAA, HSZ-300-320HOA, HSZ-300-331HSA, HSZ-300-330HUA, HSZ-300-341NHA, HSZ-300-350HUA, HSZ-300-360HUA, HSZ-300-385HUA, HSZ-300-390HUA), Zeolith L (HSZ-500-500KOA), Ferrierit (HSZ-700-720KOA, CP914C), Zeolith Beta (HSZ-900-931HOA, HSZ-900-940HOA, HSZ-900-980HOA, CP814E, CP814C, CP811C-300) und Zeolith Y (CBV 100, CBV 300, CBV 400, CBV 500, CBV 600, CBV 712, CBV 720, CBV 760, CBV 780, CBV 901), bevorzugt ZSM-5.

16. Katalysator nach einem der Ansprüche 12-15, wobei die Alkalimetallverbindungen ausgewählt sind aus der Gruppe bestehend aus Cs-Oxiden, $CsNO_3$, Cs_2SO_4, CsF, CsCl, CsBr, CsI, Cs_3PO_4, Cs_2CO_3, $Cs_2C_2O_4$, CH_3CO_2Cs (mit variierender Cs-Beladung, bevorzugt von 1 bis 60), Li-Oxiden, $LiNO_3$, Li_2SO_4, LiF, LiCl, LiBr, LiI, Li_3PO_4, Li_2CO_3, $Li_2C_2O_4$, CH_3CO_2Li (mit variierender Li-Beladung, bevorzugt von 1 bis 60), Na-Oxiden, $NaNO_3$, Na_2SO_4, NaF, NaCl, NaBr, NaI, Na_3PO_4, Na_2CO_3, $Na_2C_2O_4$, CH_3CO_2Na (mit variierender Na-Beladung, bevorzugt von 1 bis 60), K-Oxiden, KNO_3, K_2SO_4, KF, KCl, KBr, KI, K_3PO_4, K_2CO_3, $K_2C_2O_4$, CH_3CO_2K (mit variierender K-Beladung, bevorzugt von 1 bis 60), Rb-Oxiden, $RbNO_3$, Rb_2SO_4, RbF, RbCl, RbBr, RbI, Rb_3PO_4, Rb_2CO_3, $Rb_2C_2O_4$, CH_3CO_2Rb (mit variierender Rb-Beladung, bevorzugt von 1 bis 60)

17. Katalysator nach einem der vorhergehenden Ansprüche, wobei der Katalysator ausgewählt ist aus der Gruppe bestehend aus xLi-Zeolith, xNa-Zeolith, xK-Zeolith, xRb-Zeolith und xCs-Zeolith, bevorzugt xCs-ZSM-5 Alumosilikatzeolith.

18. Katalysator nach einem der Ansprüche 11-16, der bei der Herstellung von GLD aus GL in einem Gasphasen-Festbett-Durchlaufreaktor einen Umsatz des GL von mehr als 86 mol% und eine Ausbeute von GLD von über 40 mol% zeigt.

FIG. 1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Oxidation
Glycerol
OH
HO
OH
Dehydration
(b)
O
Acrolein
Hydrogenation
O
Propionaldehyde
Dehydration
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Oxidation
Hydrogenation
O
HO
Acrylic acid
O
HO
Hydroxyacetone
OH
Allyl alcohol
Hydrogenation
Epoxidation
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O
Glycidol
Oxidation
O
HO
Acetic acid

FIG. 2

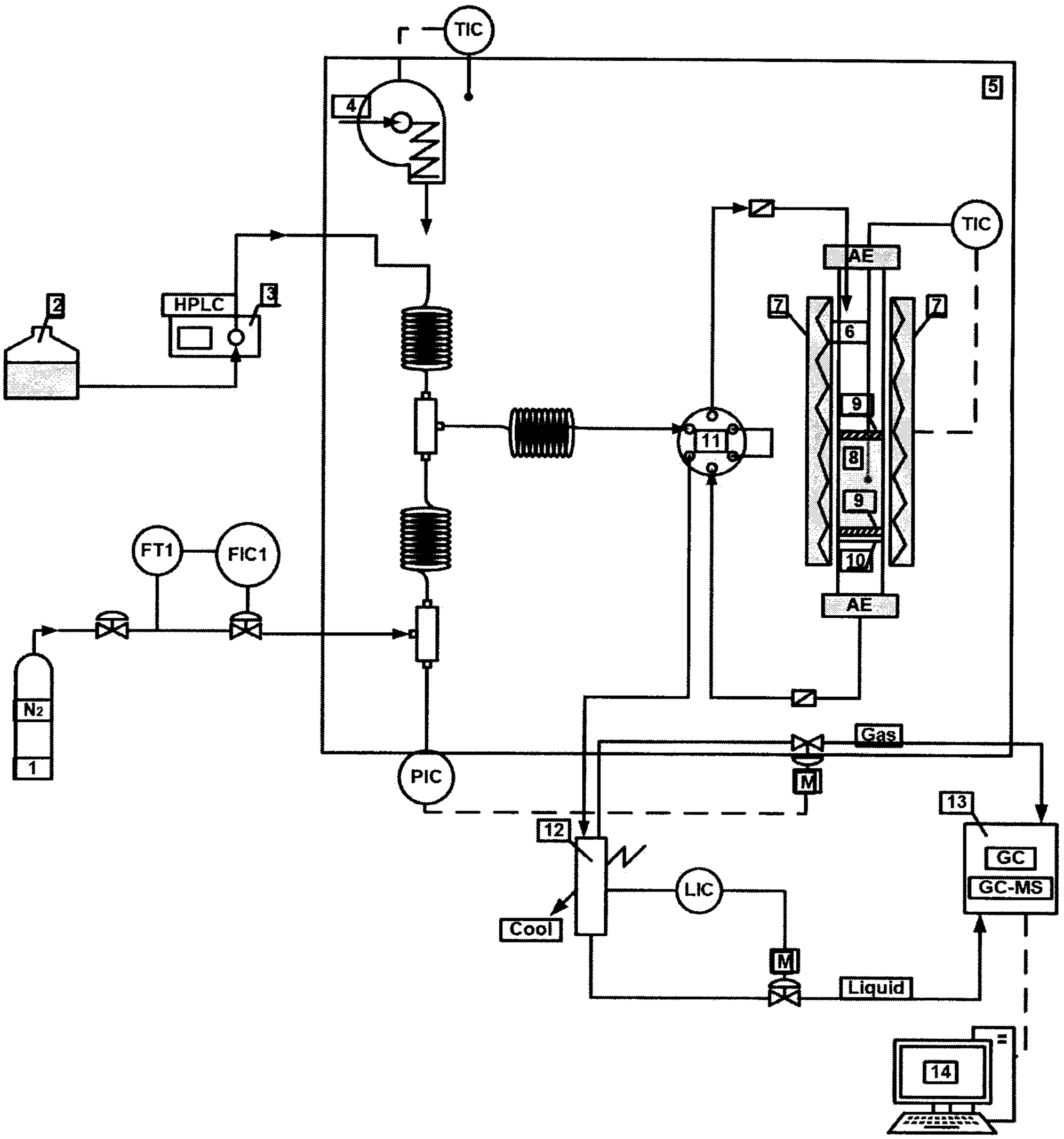
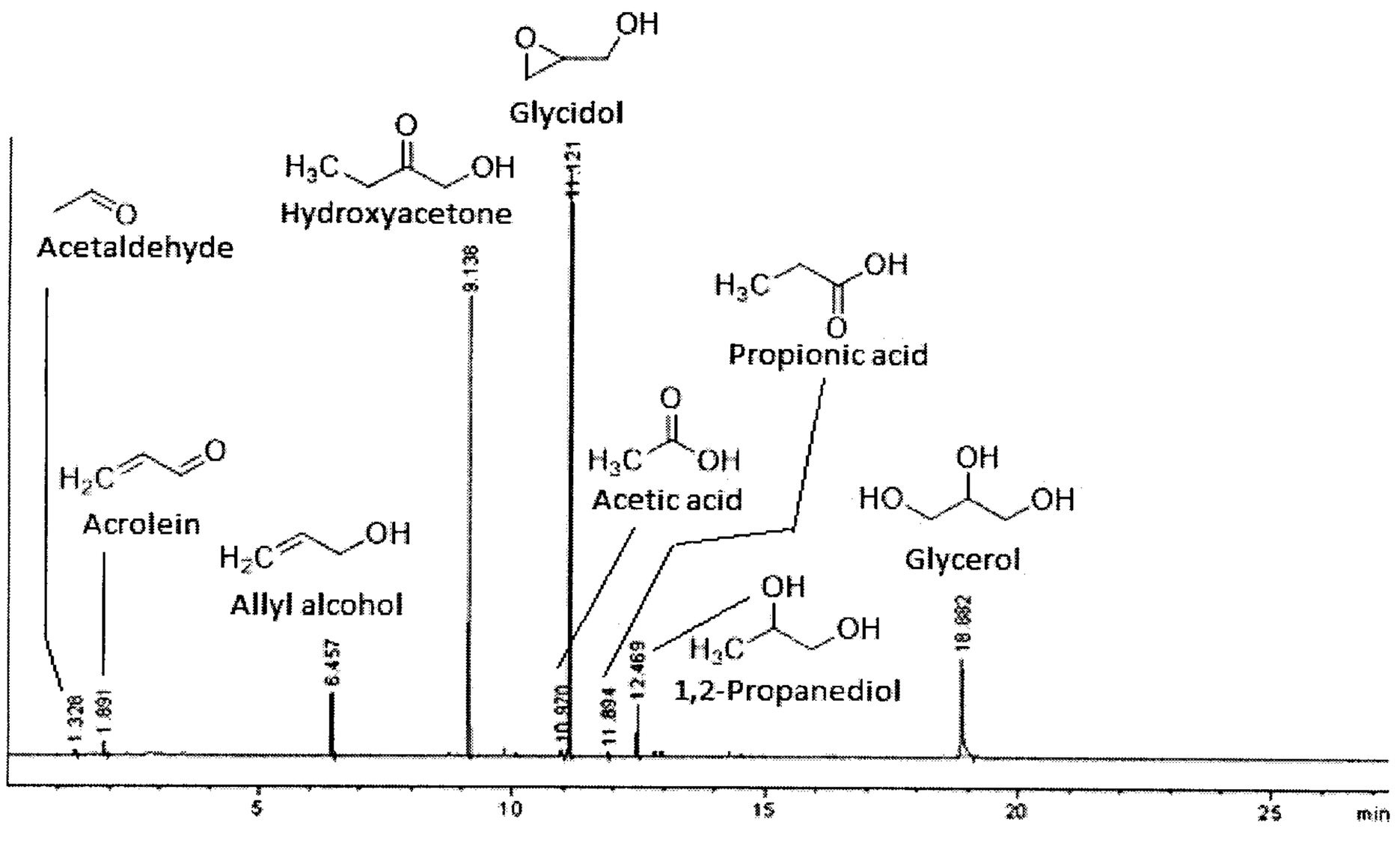

TIC
4
5
2
HPLC
3
AE
TIC
7
7
6
9
11
8
9
10
AE
FT1
FIC1
N2
1
Gas
M
PIC
13
12
GC
GC-MS
LIC
Cool
M
Liquid
14

FIG. 3


Glycidol
Hydroxyacetone
Acetaldehyde
Propionic acid
Acrolein
Acetic acid
Glycerol
Allyl alcohol
1,2-Propanediol
1.328
1.891
6.457
9.138
11.121
10.920
11.894
12.469
18.882
5
10
15
20
25
min