a) reacting propene with hydrogen peroxide in the presence of a catalyst mixture comprising a phase transfer catalyst, phosphoric acid and a heteropolytungstate in a liquid reaction mixture comprising an aqueous phase with a maximum apparent pH of 6 and an organic phase, herein the term “apparent pH” here refers to a value determined by measurement with a glass electrode employing a commercial pH meter calibrated with aqueous buffer solutions of known pH for measuring dilute aqueous solutions;

b) separating the reaction mixture into an aqueous phase (P_a) comprising 1,2-propanediol and formic acid and an organic phase (P_o);

c) recycling at least a part of the separated organic phase (P_o) to the reaction step a);

d) contacting at least a part of the aqueous phase (P_a) separated in step b) with a palladium catalyst to provide a treated aqueous phase, wherein no hydrogen is added in contacting step d); and

e) recovering 1,2-propanediol from the treated aqueous phase provided in step d).

[007] In a further aspect the present invention relates to the use of a contacting step d) to decompose formic acid in a method for the preparation of 1,2-propanediol comprising:

a) Reacting propene with hydrogen peroxide in the presence of a catalyst mixture comprising a phase transfer catalyst, phosphoric acid and a heteropolytungstate in a liquid reaction mixture comprising an aqueous phase with a maximum apparent pH of 6 and an organic phase, wherein the term “apparent pH” here refers to a value determined by measurement with a glass electrode employing a commercial pH meter calibrated with aqueous buffer solutions of known pH for measuring dilute aqueous solutions;

b) separating the reaction mixture into an aqueous phase (P_a) comprising 1,2-propanediol and formic acid and an organic phase (P_o);

c) recycling at least a part of the separated organic phase (Po) to the reaction step a);

d) contacting at least a part of the aqueous phase (P_a) separated in step b) with a palladium catalyst to provide a treated aqueous phase; and

e) recovering 1,2-propanediol from the treated aqueous phase provided in step d).

Detailed description of the invention

[008] In the method of the present invention, propene is reacted in a step a) with hydrogen peroxide in the presence of a catalyst mixture comprising a phase transfer catalyst and a heteropolytungstate. This reaction is carried out in a liquid reaction mixture which comprises an aqueous phase with a maximum apparent pH of 6 and an organic phase.

[009] Propene can be used in pure form or in a mixture with propane, wherein the proportion of propane may be up to 20 mol-%. The proportion of propane in the propene used is preferably less than 5 mol-%. Propene is preferably employed in a molar excess to hydrogen peroxide, preferably in a molar ratio of propene to hydrogen peroxide of from 1.1:1 to 10:1.

[010] Hydrogen peroxide is preferably used in the form of an aqueous solution, preferably with a hydrogen peroxide content of 10 to 80 % by weight, particularly preferably 30 to 70 % by weight.

Any commercially available grade of aqueous hydrogen peroxide solutions can be used. A crude hydrogen peroxide product obtained in the extraction stage of the anthraquinone process for producing hydrogen peroxide may also be used.

Claims:

1. A method for the preparation of 1,2-propanediol comprising:

a) reacting propene with hydrogen peroxide in the presence of a catalyst mixture comprising a phase transfer catalyst, phosphoric acid and a heteropolytungstate in a liquid reaction mixture comprising an aqueous phase with a maximum apparent pH of 6 and an organic phase, wherein the term “apparent pH” here refers to a value determined by measurement with a glass electrode employing a commercial pH meter calibrated with aqueous buffer solutions of known pH for measuring dilute aqueous solutions;

b) separating the reaction mixture into an aqueous phase (P_a) comprising 1,2-propanediol and formic acid and an organic phase (P_o);

c) recycling at least a part of the separated organic phase (P_o) to the reaction step a);

d) contacting at least a part of the aqueous phase (P_a) separated in step b) with a palladium catalyst to provide a treated aqueous phase, wherein no hydrogen is added in contacting step d); and

e) recovering 1,2-propanediol from the treated aqueous phase provided in step d).

~~2. The method of claim 1, wherein no hydrogen is added in contacting step d).~~

~~3.~~2. The method of claim 1 ~~or 2~~, wherein the contacting in step d) is conducted at a pressure sufficient to maintain a liquid aqueous phase.

~~4.~~3. The method of claim ~~3~~2, wherein the pressure in the contacting step d) is from 1 to 100 bar.

~~5.~~4. The method of any one of claims 1 to ~~4~~3, wherein the temperature in the contacting step d) is between 0 °C and 200 °C, preferably in the range of 100 °C to 180 °C.

~~6.~~5. The method of any one of claims 1 to ~~5~~4, wherein between steps b) and d) or between steps d) and e) at least a part of the aqueous phase is subjected to a step f) of catalytic hydrogenation at a temperature in the range of 80 °C to 140 °C, preferably 90 °C to 120 °C.

~~7.~~6. The method of any one of claims 1 to ~~6~~5, wherein step e) comprises a multi-step distillation, with the first distillation step and optionally further distillation steps providing an overhead product comprising water and a bottoms product which is passed to the next distillation step, and a distillation step providing an overhead product comprising 1,2-propanediol and a residuals bottoms product.

~~8.~~7. The method of claim ~~7~~6, wherein the residuals bottom product is subjected to at least one further distillation step.

~~9.~~8. The method of any one of claims 1 to ~~8~~7, wherein phosphoric acid is present in step a) and the heteropolytungstate is a polytungstophosphate.

~~10.~~9. The method of any one of claims 1 to ~~9~~8, wherein the organic phase in step a) comprises an organic solvent having a boiling point of more than 100 °C at atmospheric pressure and a solubility in water at 20 °C of less than 250 mg/kg, the organic solvent being preferably selected from alkylated aromatic hydrocarbons having 8 to 12 carbon atoms.

~~11.~~10. The method of any one of claims 1 to ~~10~~9, wherein the phase transfer catalyst is selected from tertiary amines and tertiary or quaternary ammonium salts and comprises in total at least 12 carbon atoms.

~~12.~~11. The method of claim ~~11~~10, wherein the phase transfer catalyst comprises a tertiary or quaternary ammonium ion having the structure $R^1R^2R^3NR^4{}^+$, wherein R^1, R^2 and R^3 are the same or different and are each selected from alkyl groups having from 8 to 10 carbon atoms and R^4 is hydrogen or methyl.

~~13.~~12. Use of a contacting step d) to decompose formic acid in a method for the preparation of 1,2-propanediol comprising:

a) reacting propene with hydrogen peroxide in the presence of a catalyst mixture comprising a phase transfer catalyst, phosphoric acid and a heteropolytungstate in a liquid reaction mixture comprising an aqueous phase with a maximum apparent pH of 6 and an organic phase, wherein the term “apparent pH” here refers to a value determined by measurement with a glass electrode employing a commercial pH meter calibrated with aqueous buffer solutions of known pH for measuring dilute aqueous solutions;
b) separating the reaction mixture into an aqueous phase (P_a) comprising 1,2-propanediol and phosphoric acid esters of 1,2-propanediol and an organic phase (P_o);
c) recycling at least a part of the separated organic phase (P_o) to the reaction step a);
d) contacting at least a part of the aqueous phase (P_a) separated in step b) with a palladium catalyst to provide a treated aqueous phase; and
e) recovering 1,2-propanediol from the treated aqueous phase provided in step d).

~~14.~~13. The use of claim ~~13~~12, wherein the method for the preparation of 1,2-propanediol is performed as defined in any one of claims 2 to ~~12~~11.