

Start-up Method for a Process for Preparing an Olefin Oxide

In a first aspect, the invention relates to a start-up method for a process for preparing an olefin oxide comprising a normal run stage, wherein the normal run stage comprises providing olefin, hydrogen peroxide and organic solvent into an epoxidation zone comprising an heterogeneous epoxidation catalyst, so that a reaction mixture comprising olefin, hydrogen peroxide and organic solvent is formed and subjecting the reaction mixture to epoxidation reaction conditions in the epoxidation zone, thereby obtaining a mixture comprising olefin oxide and organic solvent; wherein the start-up method comprises (a) providing olefin and organic solvent for a first period of time P_1 to the epoxidation zone, so that a first mixture 1 is formed, which is essentially free of hydrogen peroxide, and contacting the first mixture 1 over P_1 under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst; and (b) after the first period of time providing olefin, organic solvent and hydrogen peroxide to the epoxidation zone for a second period of time P_2 , so that a second mixture 2 is formed, which comprises olefin, organic solvent, and hydrogen peroxide, and contacting the second mixture 2 over P_2 under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst. A second aspect of the invention is directed to a process for preparing an olefin oxide comprising a normal run stage and a start-up stage, wherein the normal run stage comprises (A) providing olefin, hydrogen peroxide, water and organic solvent into an epoxidation zone comprising an heterogeneous epoxidation catalyst, so that a reaction mixture comprising olefin, hydrogen peroxide, water and organic solvent is formed; (B) subjecting the reaction mixture from (A) to epoxidation reaction conditions in the epoxidation zone, thereby obtaining a mixture comprising olefin oxide, water and organic solvent; and (C) removing an effluent stream from the epoxidation zone, comprising olefin oxide, water and organic solvent; wherein the start-up stage comprises steps (a) and (b) of the method of the first aspect. In a third aspect, the invention is related to an olefin oxide obtained or obtainable from the process of the second aspect.

Olefin oxides such as propylene oxide are important intermediates in the chemical industry. A suitable process for the preparation of olefin oxide starts from the respective olefin and makes use of hydrogen peroxide as oxidizing agent, organic solvents, water and heterogeneous epoxidation catalysts such as titanium containing zeolites. Due to the importance for industrial-scale processes, it is desired to carry out such epoxidation reactions as efficiently as possible.

Any process and even more important each industrial scale process comprises at least three stages, that is a start-up stage, wherein the reaction is started, a normal run stage, wherein the reaction is carried out so that the desired product is obtained, and finally a shutdown stage, where the reaction is terminated and the reaction vessel may be emptied, for example, in order to enable catalyst regeneration, replacement etc.

- The start-up stage, since it defines the conditions under which the catalyst in the reactor has to operate, is of major importance. Especially when, as it is often the case, epoxidations are carried out in several reactors in parallel, the start-up is relevant, since normally, any epoxidation process is part of a highly integrated system, wherein reactors are sequentially started and shutdown. In case one of a plurality of reactors has to be started, while one or more of the others are in operation, it is mandatory that this reactor do not negatively impair the overall balance.
- One option for starting a reactor is disclosed in WO 2017/162446 A1 (Evonik Degussa GmbH et al.), which describes a process for the epoxidation of propylene by continuously reacting propylene with hydrogen peroxide in a methanol solvent and in the presence of a shaped titanium silicalite catalyst with a start-up stage, wherein methanol solvent is fed to the reaction tubes at a feeding rate of from 50 to 100 % of a feeding rate for full load of the reactor; hydrogen peroxide is fed to the reaction tubes at a feeding rate that starts with no more than 10 % of a feeding rate for full load of the reactor and is increased continuously or stepwise to the rate for full load of the reactor and propylene is fed to the reaction tubes at a feeding rate of from 20 to 100 % of a feeding rate for full load of the reactor.
- The technical problem underlying the present invention was thus to provide an improved method for starting an epoxidation reaction.
- A first aspect of the invention is related to a start-up method for a process for preparing an olefin oxide comprising a normal run stage, wherein the normal run stage comprises providing olefin, hydrogen peroxide and organic solvent into an epoxidation zone comprising an heterogeneous epoxidation catalyst, so that a reaction mixture comprising olefin, hydrogen peroxide and organic solvent is formed and subjecting the reaction mixture to epoxidation reaction conditions in the epoxidation zone, thereby obtaining a mixture comprising olefin oxide and organic solvent; wherein the start-up method comprises
- (a) providing olefin and organic solvent for a first period of time P_1 to the epoxidation zone, so that a first mixture 1 is formed, which is essentially free of hydrogen peroxide, and contacting the first mixture 1 over P_1 under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst;
 - (b) after the first period of time providing olefin, organic solvent and hydrogen peroxide to the epoxidation zone for a second period of time P_2 , so that a second mixture 2 is formed, which comprises olefin, organic solvent, and hydrogen peroxide, and contacting the second mixture 2 over P_2 under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst.

"Essentially free of hydrogen peroxide" regarding the mixture in (a) means that said mixture comprises less than 0.2 weight-%, preferably less than 0.1 weight-%, more preferably less than 0.05 weight-%, of hydrogen peroxide, based on the total weight of the mixture.

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It was surprisingly shown that using a start-up procedure with a start of propylene feed prior to the start of hydrogen peroxide feed significantly helped to minimize the propylene oxide losses during the start-up phase, i.e. improves the selectivity towards propylene oxide, and was thus superior to a start-up procedure with start of hydrogen peroxide feed prior to start of propylene feed. Furthermore, the inventive process surprisingly results in slower catalyst deactivation over time and proves effective in reduction of by-products formation.

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In some preferred embodiments of the start-up method, the amount of olefin provided in (a) is lower than the amount intended to be provided in the normal run stage.

In some preferred embodiments of the start-up method, the amounts of olefin and of hydrogen peroxide provided in (b) are lower than the respective amounts intended to be provided in the normal run stage, wherein preferably, the molar amount of olefin provided in (b) is higher than the molar amount of hydrogen peroxide provided in (b).

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In some preferred embodiments of the start-up method, step (b) comprises

(b') after the first period of time P_1 , providing organic solvent and olefin and hydrogen peroxide in initial amounts to the epoxidation zone for a period of time P_2 , so that a mixture is formed, which comprises organic solvent, olefin, and hydrogen peroxide, wherein the amounts of the hydrogen peroxide and of the olefin are lower than the amounts intended to be provided in the normal run stage, and increasing the amount of the hydrogen peroxide and the amount of the olefin over the period of time P_2 up to the amounts intended to be provided in the normal run stage, so that a mixture 2' is formed, and contacting the mixture 2' over P_2 under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst; wherein preferably, the molar amount of olefin initially provided is higher than the molar amount of hydrogen peroxide initially provided and the molar amount of olefin provided during the increase is higher than the molar amount of hydrogen peroxide provided during the increase.

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In the mixture 2', due to the increasing of the amount of the hydrogen peroxide and the amount of the olefin over the period of time P_2 , the concentrations of hydrogen peroxide and olefin increase over P_2 .

In some preferred embodiments of the start-up method, the olefin is provided in (a) in a molar ratio relative to the molar amount of hydrogen peroxide intended to be used in the normal run stage in the range of from 0.1:1 to 4:1, preferably in the range of from 0.1:1 to 1:1 or in the range of from 2:1 to 4:1.

In some preferred embodiments of the start-up method, the olefin and the hydrogen peroxide are provided in (b) or in (b') respectively so that the molar ratio of olefin : hydrogen peroxide in the second mixture 2 formed in (b) or in the mixture formed in (b') respectively is in the range of from 1.1:1 to 5:1, preferably in the range of from 1.1:1 to 2:1 or in the range of from 3:1 to 5:1.

In the normal run stage of the process for preparing an olefin oxide, the olefin is preferably used in a molar excess compared to the hydrogen peroxide. The expression "the olefin is provided in (a) in a molar ratio relative to the molar amount of hydrogen peroxide intended to be used in the normal run stage" means for the start-up method, that per mol of hydrogen peroxide intended to be used in the normal run stage, the exceeding molar amount of olefin in relation to a 1 : 1 ratio olefin : hydrogen peroxide is provided in (a) and thus contained in the first mixture 1 formed in (a). In other words, the molar amount of olefin provided in (a) is (molar amount of hydrogen peroxide intended to be used in the normal run stage) – (molar amount of olefin intended to be used in the normal run stage). For example, in case the molar ratio olefin : hydrogen peroxide intended to be used in the normal run stage is 1.1:1, then the exceeding molar amount of olefin intended to be used in the normal run stage is 0.1.

Using a molar excess of propylene vis-à-vis hydrogen peroxide used or intended to be used in the range of from 0.1:1 to 4:1, preferably in the range of from 0.1:1 to 1:1 or in the range of from 2.1 to 4:1 in step (a) and preferably also a molar ratio of olefin : hydrogen peroxide in the second mixture 2 formed in (b) or in the mixture formed in (b') respectively is in the range of from 1.1:1 to 5:1, preferably in the range of from 1.1:1 to 2:1 or in the range of from 3:1 to 5:1, surprisingly gives an improved performance in that the selectivity towards olefin oxide formed in step (b) (removed as described in more detail below in (b.2) or (b'.2)) from the can be maintained, while the selectivities with respect to four of the main by-products, namely acetaldehyde (AA), 1-methoxy-2-propanol (PM-2), 2-methoxy-1-propanol (PM-1), hydroxyacetone (acetol), are drastically reduced, compared to a process variant where said specific excess ratio is not applied.

The point in time when step (a) starts is t_1 , while the point in time when step (b) or (b') starts is t_2 . The first period of time P_1 is thus the period of time between t_2 and t_1 , i.e. $P_1 = t_2 - t_1$. When the amounts of all components (olefin, organic solvent and hydrogen peroxide) are as high as

intended for the normal run stage, this indicates the beginning of the normal run stage, which happens at a point in time t_3 . The second period of time P_2 or $P_{2'}$ in case of (b') is thus the period of time between t_3 and t_2 , i.e. $P_2 = t_3 - t_2$ (or $P_{2'} = t_3 - t_2$).

- 5 The molar amounts of hydrogen peroxide and olefin initially provided in (b') are preferably each in the range of from 1 to 50% of the amount intended to be used in the normal run stage. During $P_{2'}$, the amounts of hydrogen peroxide and of olefin are increased up to 100% of the amounts intended to be used in the normal run stage, wherein the increasing is carried out stepwise or continuously, so that the mixture formed in (b') comprises increasing amounts of olefin and hydrogen peroxide compared to the amounts initially provided in (b'), while the molar ratio of olefin : hydrogen peroxide during P_2 or $P_{2'}$ is preferably maintained in the range of from 1.1:1 to 5:1, preferably in the range of from 1.1:1 to 2:1 or in the range of from 3:1 to 5:1.

- As indicated also below, the amount of hydrogen peroxide provided in the normal run stage is adjusted so that the molar ratio of olefin : hydrogen peroxide in the reaction mixture formed is in the range of from 1.1:1 to 5:1, preferably in the range of from 1.1:1 to 2:1 or in the range of from 3:1 to 5:1. Therefore, in (b), (b') preferably an excess of olefin compared to hydrogen peroxide is used, wherein in (a), only the exceeding molar amount of olefin compared to the molar amount of hydrogen peroxide – in relation to what is intended to be used in the normal run stage – is provided.

In some preferred embodiments of the start-up method, (a) comprises

- (a.1) providing olefin and organic solvent for a first period of time P_1 to the epoxidation zone, so that a first mixture 1 is formed, which is essentially free of hydrogen peroxide, and contacting the first mixture 1 over P_1 under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst;
- (a.2) removing during P_1 an effluent stream from the epoxidation zone, the effluent stream comprising olefin and organic solvent.
- Step (a.2) is directly connected to (a.1).

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In some preferred embodiments of the start-up method, (b) comprises

- (b.1) after the first period of time providing olefin, organic solvent and hydrogen peroxide to the epoxidation zone for a second period of time P_2 , so that a second mixture 2 is formed, which comprises olefin, organic solvent, and hydrogen peroxide, and contacting the second mixture 2 over P_2 under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst;
- (b.2) removing during the respective period of time an effluent stream from the epoxidation zone, the effluent stream comprising olefin oxide and organic solvent;

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and/or wherein (b') comprises

(b'.1) after the first period of time P_1 , providing organic solvent and olefin and hydrogen peroxide in initial amounts to the epoxidation zone for a period of time P_2 , so that a mixture is formed, which comprises organic solvent, olefin, and hydrogen peroxide, wherein the amounts of the hydrogen peroxide and of the olefin are lower than the amounts intended to be provided in the normal run stage, and increasing the amount of the hydrogen peroxide and the amount of the olefin over the period of time P_2 up to the amounts intended to be provided in the normal run stage, so that a mixture 2' is formed, and contacting the mixture 2' over P_2 under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst;

(b'.2) removing during the respective period of time an effluent stream from the epoxidation zone, the effluent stream comprising olefin oxide and organic solvent.

Step (b.2) or (b'.2) is directly connected to (b.1), or (b'.1).

15 *Additive*

In some preferred embodiments of the start-up method in any one of (a), (a.1), (b), (b'), (b.1), (b'.1), preferably in at least one of (b), (b'), (b.1), (b'.1), more preferably in each of (b), (b'), (b.1), (b'.1), an additive is provided to the epoxidation zone, wherein the additive is selected from the group consisting of potassium salt of an inorganic acid, potassium salt of an organic acid, ammonia, ammonium salt of an inorganic acid, ammonium salt of an organic acid and mixtures of two or more thereof;

wherein the additive is preferably selected from the group consisting of potassium dihydrogen phosphate, dipotassium hydrogen phosphate, potassium formate, potassium acetate, potassium hydrogen carbonate, dipotassium etidronate, ammonium dihydrogen phosphate, diammonium hydrogen phosphate, ammonia and mixtures of two or more thereof,

more preferably from the group consisting of potassium dihydrogen phosphate, dipotassium hydrogen phosphate, dipotassium etidronate, ammonia and mixtures of two or more thereof;

wherein the additive more preferably comprises at least dipotassium etidronate or dipotassium hydrogen phosphate or a mixture of dipotassium etidronate and dipotassium hydrogen phosphate, wherein more preferably in the range of from 95 to 100 weight-% of the additive are dipotassium etidronate or dipotassium hydrogen phosphate or a mixture of dipotassium etidronate and dipotassium hydrogen phosphate.

- Preferably, the additive is in case of ammonia provided in pure form or in aqueous solution, wherein the additive is in case of being selected from the group consisting of potassium salt of an inorganic acid, potassium salt of an organic acid, ammonium salt of an inorganic acid, ammonium salt of an organic acid or any mixture comprising two or more thereof or any mixture comprising ammonia and at least one thereof provided in aqueous solution;
- wherein the additive in aqueous solution releases or forms one or more cation(s) M, wherein M represents in case of a potassium salt K^+ , or, in case of ammonia or ammonium salts, M represents the sum of NH_4^+ and NH_3 .
- Etidronic acid is a tetrabasic acid with pKs values of 1.35 ± 0.08 ; 2.87; 7.03 ± 0.01 ; 11.3. Each of the above-mentioned ammonia, potassium salts and ammonium salts, when in aqueous solution, dissociates to release or forms at least to some extent anion(s) and one or more cation(s). For example, ammonia forms to some extent NH_4^+ , ammonium salts dissociate to some extent to NH_4^+ and one or more anion(s), or potassium salts dissociate to some extent to release K^+ and one or more anion(s), the positive charge compensated by the appropriate equivalent of anion(s)). Regarding ammonia and ammonium salts, due to the dissociation equilibrium between NH_3 and NH_4^+ , the sum of NH_3 and NH_4^+ has to be considered for M. In some preferred embodiments, the aqueous solution of additive comprises in the range of from 0.01 to 5 weight-%, preferably in the range of from 0.5 to 3 weight-%, more preferably in the range of from 1 to 2 weight-%, of additive, based on the overall weight of the aqueous solution.

In some preferred embodiments of the start-up method, the additive is preferably pre-mixed with the organic solvent or with the hydrogen peroxide, preferably with the organic solvent, prior to being provided to the epoxidation zone. In some preferred embodiments of the start-up method, the additive is provided in any one of (a), (b), (b'), (a.1), (b.1), (b'.1), preferably in at least in any one of (b), (b'), (b.1), (b'.1), more preferably in each of (b), (b'), (b.1), (b'.1), in a molar ratio M : hydrogen peroxide in the range of from 1×10^{-5} : 1 to 1×10^{-3} : 1. When additive is provided in (a), then the molar ratio M : hydrogen peroxide applies for the hydrogen peroxide intended to be provided in the normal run stage.

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Periods of time

In some preferred embodiments of the start-up method, the first period of time P_1 is preferably a period of time in the range of from 1 minutes to 5 hours, more preferably in the range of from 5 minutes to 1 hour, more preferably in the range of from 10 minutes to 30 minutes; and/or wherein the second period of time P_2 or P_2' respectively is preferably a period of time in the range of from 30 minutes to 24 hours, more preferably in the range of from 2 to 18 hours, more preferably in the range of from 4 to 12 hours.

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In some preferred embodiments the start-up method further comprising before (a)
(x) providing an organic solvent stream for a period of time P_x to the epoxidation zone,
wherein P_x is preferably a period of time in the range of from 10 minutes to 24 hours.

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The organic solvent stream provided in (x) is essentially free of olefin and of hydrogen peroxide,
wherein "essentially free of" means that the respective compound is contained in said stream in
less than 0.2 weight-%, preferably less than 0.1 weight-%, more preferably less than
0.05 weight-%, based on the total weight of the stream. Preferably the organic solvent stream
provided in (x) is also essentially free of additive, wherein "essentially free of" means that the
additive is contained in said stream in less than 0.2 weight-%, preferably less than 0.1 weight-
%, more preferably less than 0.05 weight-%, based on the total weight of the stream. In some
preferred embodiments, the organic solvent is provided in each of (a), (b), (a.1), (a.2), and (b')
in the range of from 50 to 100%, preferably in the range of from 70 to 100%, more preferably in
the range of from 90 to 100%, of the amount as intended to be used in the normal run stage.

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Reaction conditions

In some preferred embodiments the start-up method is carried out continuously.

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In some preferred embodiments of the start-up method, the contacting under epoxidation reac-
tion conditions in the epoxidation zone with the heterogeneous epoxidation catalyst is carried
out at an absolute pressure in the epoxidation zone in the range of from 0.5 to 5.0 MPa, prefera-
bly in the range of from 1.5 to 3.0 MPa, more preferably in the range of from 1.8 to 2.8 MPa.

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In some preferred embodiments of the start-up method, the contacting under epoxidation reac-
tion conditions in the epoxidation zone with the heterogeneous epoxidation catalyst is carried
out at a temperature in the epoxidation zone in the range of from 20 to 75 °C, preferably in the
range of from 22 to 75 °C, more preferably in the range of from 24 to 70 °C, more preferably in
the range of from 25 to 65 °C.

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In some preferred embodiments of the start-up method, the epoxidation reaction conditions
comprise trickle bed conditions.

In some preferred alternative embodiments of the start-up method, the epoxidation reaction
conditions comprise fixed bed conditions.

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Catalyst

In some preferred embodiments of the start-up method, the heterogeneous epoxidation catalyst comprises a zeolitic material having a framework structure comprising Si, O and Ti.

- 5 In some preferred embodiments of the start-up method, the zeolitic material comprises Ti in an amount in the range of from 0.2 to 5 weight-%, preferably in the range of from 0.5 to 4 weight-%, more preferably in the range of from 0.7 to 3 weight-%, calculated as elemental Ti and based on the total weight of the zeolitic material.
- 10 In some preferred embodiments of the start-up method, the zeolitic material having a framework structure comprising Si, O and Ti comprised in the epoxidation catalyst is a titanium zeolite having ABW, ACO, AEI, AEL, AEN, AET, AFG, AFI, AFN, AFO, AFR, AFS, AFT, AFX, AFY, AHT, ANA, APC, APD, AST, ASV, ATN, ATO, ATS, ATT, ATV, AWO, AWW, BCT, BEA, BEC, BIK, BOG, BPH, BRE, CAN, CAS, CDO, CFI, CGF, CGS, CHA, CHI, CLO, CON, CZP, DAC, DDR,
- 15 DFO, DFT, DOH, DON, EAB, EDI, EMT, EPI, ERI, ESV, ETR, EUO, FAU, FER, FRA, GIS, GIU, GME, GON, GOO, HEU, IFR, ISV, ITE, ITH, ITQ, ITW, IWR, IWW, JBW, KFI, LAU, LEV, LIO, LOS, LOV, LTA, LTL, LTN, MAR, MAZ, MCM-22(S), MCM-36, MCM-56, MEI, MEL, MEP, MER, MIT-1, MMFI, MFS, MON, MOR, MSE, MSO, MTF, MTN, MTT, MTW, MWW, NAB, NAT, NEES, NON, NPO, OBW, OFF, OSI, OSO, PAR, PAU, PHI, PON, RHO, RON, RRO, RSN,
- 20 RTE, RTH, RUT, RWR, RWY, SAO, SAS, SAT, SAV, SBE, SBS, SBT, SFE, SFF, SFG, SFH, SFN, SFO, SGT, SOD, SSY, STF, STI, STT, TER, THO, TON, TSC, UEI, UFI, UOZ, USI, UTL, VET, VFI, VNI, VSV, WEI, WEN, YUG, ZON, SVR, SVY framework structure or a mixed structure of two or more of these framework types; more preferably the zeolitic material having a framework structure comprising Si, O and Ti is a titanium zeolite having an MFI framework type,
- 25 an MEL framework type, an MWW framework type, an MCM-22(S) framework type, an MCM-56 framework type, an IEZ-MWW framework type, an MCM-36 framework type, an ITQ framework type, a BEA framework type, a MOR framework type, or a mixed structure of two or more of these framework types; more preferably the zeolitic material having a framework structure comprising Si, O and Ti is a titanium zeolite having an MFI framework type, or an MWW framework
- 30 type; more preferably the zeolitic material having a framework structure comprising Si, O and Ti has framework type MFI; more preferably the zeolitic material having a framework structure comprising Si, O and Ti is a titanium silicalite-1 (TS-1).

- In some preferred embodiments of the start-up method, the heterogeneous epoxidation catalyst
- 35 further comprises a binder, which preferably comprises silicon dioxide.

In some preferred embodiments of the start-up method, the heterogeneous epoxidation catalyst is in the form of a molding, preferably in the form of a strand or a granule. A strand has a cross

section wherein the cross section preferably has a hexagonal, rectangular, quadratic, triangular, trilobe, oval, or circular shape. In some preferred embodiments, the molding has the form of a strand having a circular cross-section, which is more preferably formed by extrusion (cylindrical extrudate). A granule preferably comprises particles having a form selected from cylinder, sphere, trilobe (particle having a trilobe cross section), and mixed forms of two or more of these forms, wherein the granule comprises particles of one form as well as mixtures of particles having two or more of these forms. A "sphere" comprises an ideal sphere form but also spheroidal forms. A "cylinder" comprises forms having a high h which is larger than the radius of the circle area as well as forms having a high h which is smaller than the radius of the circle area (tablet form).

In some preferred embodiments of the start-up method, from 95 to 100 weight-%, preferably from 98 to 100 weight-%, more preferably from 99 to 100 weight-%, more preferably from 99.5 to 100 weight-%, more preferably from 99.9 to 100 weight-% of the molding consist of the zeolitic material and the binder.

In some preferred embodiments of the start-up method, from 95 to 100 weight-%, preferably from 98 to 100 weight-%, more preferably from 99 to 100 weight-%, more preferably from 99.5 to 100 weight-%, more preferably from 99.9 to 100 weight-% of the binder comprised in the molding consist of Si and O.

In some preferred embodiments of the start-up method, the heterogeneous epoxidation catalyst, preferably the molding, comprises the binder, calculated as SiO_2 , in an amount in the range of from 1 to 95 weight-%, preferably in the range of from 3 to 70 weight-%, more preferably in the range of from 5 to 50 weight-%, more preferably in the range of from 10 to 30 weight-%, based on the total weight of the epoxidation catalyst, preferably based on the total weight of the molding and/or wherein the heterogeneous epoxidation catalyst, preferably the molding, comprises the zeolitic material in an amount in the range of from 5 to 99 weight-%, preferably in the range of from 30 to 97 weight-%, more preferably in the range of from 50 to 95 weight-%, more preferably in the range of from 70 to 90 weight-%, based on the total weight of the heterogeneous epoxidation catalyst, preferably based on the total weight of the molding.

Hydrogen peroxide

In some preferred embodiments of the start-up method, the hydrogen peroxide is provided as aqueous hydrogen peroxide solution, which preferably has a total organic carbon content (TOC) in the range of from 100 to 800 mg per kg hydrogen peroxide comprised in the aqueous hydrogen peroxide solution, preferably in the range of from 120 to 750 mg per kg hydrogen peroxide

comprised in the aqueous hydrogen peroxide solution, more preferably in the range of from 150 to 700 mg per kg hydrogen peroxide comprised in the aqueous hydrogen peroxide solution, determined according to DIN EN 1484 (April 2019).

5 In some preferred embodiments of the start-up method, the hydrogen peroxide has a pH in the range of from 0 to 3.0, preferably in the range of from 0.1 to 2.5, more preferably in the range of from 0.5 to 2.3, determined with a pH sensitive glass electrode according to CEFIC PEROXY-GENS H₂O₂ AM-7160 standard (2003).

10 In some preferred embodiments of the start-up method, the hydrogen peroxide comprises from 20 to 85 weight-%, preferably from 30 to 75 weight-%, more preferably from 40 to 70 weight-% of hydrogen peroxide, relative to the total weight of the aqueous hydrogen peroxide solution.

In some preferred embodiments of the start-up method, the hydrogen peroxide is obtained or
15 obtainable from an anthraquinone process.

Solvent

In some preferred embodiments of the start-up method, the organic solvent is an organic epoxi-
20 dation solvent, preferably the organic solvent is selected from the group consisting of alcohol, acetonitrile, propionitrile and mixtures of two or more thereof; more preferably selected from the group consisting of alcohol, acetonitrile and mixtures of alcohol and acetonitrile; more preferably the organic solvent comprises at least an alcohol, wherein the alcohol is preferably a C₁ to C₅ mono alcohol or a mixture of two or more C₁ to C₅ alcohols, more preferably the alcohol com-
25 prises at least methanol, wherein the organic solvent more preferably comprises at least 90 weight-%, more preferably at least 95 weight-%, more preferably at least 98 weight-%, more preferably at least 99 weight-%, of methanol.

Olefin (oxide)

30 In some preferred embodiments of the start-up method, the olefin is a C₂-C₁₀ alkene, preferably a C₂-C₅ alkene, more preferably a C₂-C₄ alkene, more preferably ethylene or propylene, more preferably propylene. The olefin oxide, especially the olefin oxide removed from the epoxidation zone with the effluent stream comprising olefin oxide, water and organic solvent in (C) as de-
35 scribed in more detail below, is a C₂-C₁₀ alkene oxide, preferably a C₂-C₅ alkene oxide, more preferably a C₂-C₄ alkene oxide, more preferably ethylene oxide or propylene oxide, more preferably propylene oxide.

2nd aspect - process for preparing an olefin oxide

A second aspect of the invention is related to a process for preparing an olefin oxide comprising a normal run stage and a start-up stage, wherein the normal run stage comprises

- 5 (A) providing olefin, hydrogen peroxide, water and organic solvent into an epoxidation zone comprising an heterogeneous epoxidation catalyst, so that a reaction mixture comprising olefin, hydrogen peroxide, water and organic solvent is formed;
- (B) subjecting the reaction mixture from (A) to epoxidation reaction conditions in the epoxidation zone, thereby obtaining a mixture comprising olefin oxide, water and organic solvent;
- 10 (C) removing an effluent stream from the epoxidation zone, comprising olefin oxide, water and organic solvent;

wherein the start-up stage comprises

- (a) providing olefin and organic solvent for a first period of time P_1 to the epoxidation zone, so that a first mixture 1 is formed, which is essentially free of hydrogen peroxide, and contacting the first mixture 1 over P_1 under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst;
- 15 (b) after the first period of time providing organic solvent, olefin and hydrogen peroxide to the epoxidation zone for a second period of time P_2 , so that a second mixture 2 is formed, which comprises olefin, organic solvent, and hydrogen peroxide, and contacting the second mixture 2 over P_2 under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst.
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“Essentially free of hydrogen peroxide” regarding the mixture in (a) means that said mixture comprises less than 0.2 weight-%, preferably less than 0.1 weight-%, more preferably less than 0.05 weight-%, of hydrogen peroxide, based on the total weight of the mixture. All details, preferred embodiments and alternative preferred embodiments indicated above in the section related to the first aspect apply also for the second aspect, especially for the start-up stage comprised in the process for preparing an olefin oxide.

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30 In some preferred embodiments of the process for preparing an olefin oxide comprising a normal run stage and a start-up stage, the amount of olefin provided in (a) is lower than the amount intended to be provided in the normal run stage.

In some preferred embodiments of the process for preparing an olefin oxide comprising a normal run stage and a start-up stage, the amounts of olefin and of hydrogen peroxide provided in (b) are lower than the respective amounts intended to be provided in the normal run stage, wherein preferably, the molar amount of olefin provided in (b) is higher than the molar amount of hydrogen peroxide provided in (b).

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In some preferred embodiments of the process for preparing an olefin oxide comprising a normal run stage and a start-up stage, step (b) comprises

- (b') after the first period of time P_1 , providing organic solvent and olefin and hydrogen peroxide in initial amounts to the epoxidation zone for a period of time $P_{2'}$, so that a mixture is formed, which comprises organic solvent, olefin, and hydrogen peroxide, wherein the amounts of the hydrogen peroxide and of the olefin are lower than the amounts intended to be provided in the normal run stage, and increasing the amount of the hydrogen peroxide and the amount of the olefin over the period of time $P_{2'}$ up to the amounts intended to be provided in the normal run stage, so that a mixture 2' is formed, and contacting the mixture 2' over $P_{2'}$ under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst; wherein preferably, the molar amount of olefin initially provided is higher than the molar amount of hydrogen peroxide initially provided and the molar amount of olefin provided during the increase is higher than the molar amount of hydrogen peroxide provided during the increase.

In the mixture 2', due to the increasing of the amount of the hydrogen peroxide and the amount of the olefin over the period of time $P_{2'}$, the concentrations of hydrogen peroxide and olefin increase over $P_{2'}$.

In some preferred embodiments of the process for preparing an olefin oxide comprising a normal run stage and a start-up stage, the olefin is provided in (a) in a molar ratio relative to the molar amount of hydrogen peroxide intended to be used in the normal run stage in the range of from 0.1:1 to 4:1, preferably in the range of from 0.1:1 to 1:1 or in the range of from 2:1 to 4:1.

In some preferred embodiments of the process for preparing an olefin oxide comprising a normal run stage and a start-up stage, the olefin and the hydrogen peroxide are provided in (b) or in (b') respectively so that the molar ratio of olefin : hydrogen peroxide in the second mixture 2 formed in (b) or in the mixture formed in (b') respectively is in the range of from 1.1:1 to 5:1, preferably in the range of from 1.1:1 to 2:1 or in the range of from 3:1 to 5:1.

In the normal run stage of the process for preparing an olefin oxide, the olefin is preferably used in a molar excess compared to the hydrogen peroxide. The expression "the olefin is provided in (a) in a molar ratio relative to the molar amount of hydrogen peroxide intended to be used in the normal run stage" means for the start-up method, that per mol of hydrogen peroxide intended to be used in the normal run stage, the exceeding molar amount of olefin in relation to a 1 : 1 ratio olefin : hydrogen peroxide is provided in (a) and thus contained in the first mixture 1 formed in

(a). In other words, the molar amount of olefin provided in (a) is (molar amount of hydrogen peroxide intended to be used in the normal run stage) – (molar amount of olefin intended to be used in the normal run stage). For example, in case the molar ratio olefin : hydrogen peroxide intended to be used in the normal run stage is 1.1:1, then the exceeding molar amount of olefin intended to be used in the normal run stage is 0.1.

The point in time when step (a) starts is t_1 , while the point in time when step (b) or (b') starts is t_2 . The first period of time P_1 is thus the period of time between t_2 and t_1 , i.e. $P_1 = t_2 - t_1$. When the amounts of all components (olefin, organic solvent and hydrogen peroxide) are as high as intended for the normal run stage, this indicates the beginning of the normal run stage, which happens at a point in time t_3 . The second period of time P_2 or $P_{2'}$ in case of (b') is thus the period of time between t_3 and t_2 , i.e. $P_2 = t_3 - t_2$ (or $P_{2'} = t_3 - t_2$).

The molar amounts of hydrogen peroxide and olefin initially provided in (b') are preferably each in the range of from 1 to 50% of the amount intended to be used in the normal run stage. During $P_{2'}$, the amounts of hydrogen peroxide and of olefin are increased up to 100% of the amounts intended to be used in the normal run stage, wherein the increasing is carried out stepwise or continuously, so that the mixture formed in (b') comprises increasing amounts of olefin and hydrogen peroxide compared to the amounts initially provided in (b'), while the molar ratio of olefin : hydrogen peroxide during P_2 or $P_{2'}$ is preferably maintained in the range of from 1.1:1 to 5:1, preferably in the range of from 1.1:1 to 2:1 or in the range of from 3:1 to 5:1.

As indicated also below, the amount of hydrogen peroxide provided in the normal run stage is adjusted so that the molar ratio of olefin : hydrogen peroxide in the reaction mixture formed is in the range of from 1.1:1 to 5:1, preferably in the range of from 1.1:1 to 2:1 or in the range of from 3:1 to 5:1. Therefore, in (b), (b') preferably an excess of olefin compared to hydrogen peroxide is used, wherein in (a), only the exceeding molar amount of olefin compared to the molar amount of hydrogen peroxide – in relation to what is intended to be used in the normal run stage – is provided.

In some preferred embodiments of the process for preparing an olefin oxide comprising a normal run stage and a start-up stage, step (a) comprises

- (a.1) providing olefin and organic solvent for a first period of time P_1 to the epoxidation zone, so that a first mixture 1 is formed, which is essentially free of hydrogen peroxide, and contacting the first mixture 1 over P_1 under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst;
- (a.2) removing during P_1 an effluent stream from the epoxidation zone, the effluent stream comprising olefin and organic solvent.

Step (a.2) is directly connected to (a.1).

In some preferred embodiments of the process for preparing an olefin oxide comprising a normal run stage and a start-up stage, step (b) comprises

- 5 (b.1) after the first period of time providing olefin, organic solvent and hydrogen peroxide to the epoxidation zone for a second period of time P_2 , so that a second mixture 2 is formed, which comprises olefin, organic solvent, and hydrogen peroxide, and contacting the second mixture 2 over P_2 under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst;
- 10 (b.2) removing during the respective period of time an effluent stream from the epoxidation zone, the effluent stream comprising olefin oxide and organic solvent;
- and/or wherein (b') comprises
- (b'.1) after the first period of time P_1 , providing organic solvent and olefin and hydrogen peroxide in initial amounts to the epoxidation zone for a period of time $P_{2'}$, so that a mixture is
- 15 formed, which comprises organic solvent, olefin, and hydrogen peroxide, wherein the amounts of the hydrogen peroxide and of the olefin are lower than the amounts intended to be provided in the normal run stage, and
- increasing the amount of the hydrogen peroxide and the amount of the olefin over the period of time $P_{2'}$ up to the amounts intended to be provided in the normal run stage, so that
- 20 a mixture 2' is formed, and contacting the mixture 2' over $P_{2'}$ under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst;
- (b'.2) removing during the respective period of time an effluent stream from the epoxidation zone, the effluent stream comprising olefin oxide and organic solvent.

Step (b.2) or (b'.2) is directly connected to (b.1), or (b'.1).

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Additive

- In some preferred embodiments of the process for preparing an olefin oxide comprising a normal run stage and a start-up stage, in any one of (a), (a.1), (b), (b'), (b.1), (b'.1), preferably in at
- 30 least one of (b), (b'), (b.1), (b'.1), more preferably in each of (b), (b'), (b.1), (b'.1), an additive is provided to the epoxidation zone, wherein the additive is selected from the group consisting of potassium salt of an inorganic acid, potassium salt of an organic acid, ammonia, ammonium salt of an inorganic acid, ammonium salt of an organic acid and mixtures of two or more thereof;
- 35 wherein the additive is preferably selected from the group consisting of potassium dihydrogen phosphate, dipotassium hydrogen phosphate, potassium formate, potassium acetate, potassium hydrogen carbonate, dipotassium etidronate, ammonium dihydrogen phosphate, diammonium hydrogen phosphate, ammonia and mixtures of two or more thereof,

more preferably form the group consisting of potassium dihydrogen phosphate, dipotassium hydrogen phosphate, dipotassium etidronate, ammonia and mixtures of two or more thereof;

- 5 wherein the additive more preferably comprises at least dipotassium etidronate or dipotassium hydrogen phosphate or a mixture of dipotassium etidronate and dipotassium hydrogen phosphate, wherein more preferably in the range of from 95 to 100 weight-% of the additive are dipotassium etidronate or dipotassium hydrogen phosphate or a mixture of dipotassium etidronate and dipotassium hydrogen phosphate.

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Preferably, the additive is in case of ammonia provided in pure form or in aqueous solution, wherein the additive is in case of being selected from the group consisting of potassium salt of an inorganic acid, potassium salt of an organic acid, ammonium salt of an inorganic acid, ammonium salt of an organic acid or any mixture comprising two or more thereof or any mixture

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comprising ammonia and at least one thereof provided in aqueous solution;

wherein the additive in aqueous solution releases or forms one or more cation(s) M, wherein M represents in case of a potassium salt K^+ , or, in case of ammonia or ammonium salts, M represents the sum of NH_4^+ and NH_3 .

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Etidronic acid is a tetrabasic acid with pKs values of 1.35 ± 0.08 ; 2.87; 7.03 ± 0.01 ; 11.3. Each of the above-mentioned ammonia, potassium salts and ammonium salts, when in aqueous solution, dissociates to release or forms at least to some extent anion(s) and one or more cation(s). For example, ammonia forms to some extent NH_4^+ , ammonium salts dissociate to some extent to NH_4^+ and one or more anion(s), or potassium salts dissociate to some extent to release K^+

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and one or more anion(s), the positive charge compensated by the appropriate equivalent of anion(s)). Regarding ammonia and ammonium salts, due to the dissociation equilibrium between NH_3 and NH_4^+ , the sum of NH_3 and NH_4^+ has to be considered for M. In some preferred embodiments, the aqueous solution of additive comprises in the range of from 0.01 to 5 weight-%, preferably in the range of from 0.5 to 3 weight-%, more preferably in the range of from 1 to 2 weight-

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%, of additive, based on the overall weight of the aqueous solution.

Preferably, the additive is preferably pre-mixed with the organic solvent or with the hydrogen peroxide, preferably with the organic solvent, prior to being provided to the epoxidation zone.

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In some preferred embodiments of the process for preparing an olefin oxide comprising a normal run stage and a start-up stage, the additive is provided in any one of (a), (b), (b'), (a.1), (b.1), (b'.1), preferably in at least in any one of (b), (b'), (b.1), (b'.1), more preferably in each of

(b), (b'), (b.1), (b'.1), in a molar ratio M : hydrogen peroxide in the range of from 1×10^{-5} : 1 to 1×10^{-3} : 1.

When additive is provided in (a), then the molar ratio M : hydrogen peroxide applies for the hydrogen peroxide intended to be provided in the normal run stage.

Periods of time

In some preferred embodiments of the process for preparing an olefin oxide comprising a normal run stage and a start-up stage, the first period of time P_1 is preferably a period of time in the range of from 1 minutes to 5 hours, more preferably in the range of from 5 minutes to 1 hour, more preferably in the range of from 10 minutes to 30 minutes; and/or wherein the second period of time P_2 or P_2' respectively is preferably a period of time in the range of from 30 minutes to 24 hours, more preferably in the range of from 2 to 18 hours, more preferably in the range of from 4 to 12 hours.

In some preferred embodiments of the process for preparing an olefin oxide comprising a normal run stage and a start-up stage, the process further comprises before (a)

(x) providing an organic solvent stream for a period of time P_x to the epoxidation zone, wherein P_x is preferably a period of time in the range of from 10 minutes to 24 hours.

The organic solvent stream provided in (x) is essentially free of olefin and of hydrogen peroxide, wherein "essentially free of" means that the respective compound is contained in said stream in less than 0.2 weight-%, preferably less than 0.1 weight-%, more preferably less than 0.05 weight-%, based on the total weight of the stream. Preferably the organic solvent stream provided in (x) is also essentially free of additive, wherein "essentially free of" means that the additive is contained in said stream in less than 0.2 weight-%, preferably less than 0.1 weight-%, more preferably less than 0.05 weight-%, based on the total weight of the stream. In some preferred embodiments, the organic solvent is provided in each of (a), (b), (a.1), (a.2), and (b') in the range of from 50 to 100%, preferably in the range of from 70 to 100%, more preferably in the range of from 90 to 100%, of the amount as intended to be used in the normal run stage.

Reaction conditions

In some preferred embodiments of the process for preparing an olefin oxide comprising a normal run stage and a start-up stage, the process is carried out continuously, i.e. preferably, the normal run stage and the start-up stage are carried out continuously.

In some preferred embodiments of the process for preparing an olefin oxide comprising a normal run stage and a start-up stage, the contacting under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst is carried out at an absolute pressure in the epoxidation zone in the range of from 0.5 to 5.0 MPa, preferably in the range of from 1.5 to 3.0 MPa, more preferably in the range of from 1.8 to 2.8 MPa.

In some preferred embodiments of the process for preparing an olefin oxide comprising a normal run stage and a start-up stage, the contacting under epoxidation reaction conditions in the epoxidation zone in with the heterogeneous epoxidation catalyst is carried out at a temperature in the epoxidation zone in the range of from 20 to 75 °C, preferably in the range of from 22 to 75 °C, more preferably in the range of from 24 to 70 °C, more preferably in the range of from 25 to 65 °C.

In some preferred embodiments of the process for preparing an olefin oxide comprising a normal run stage and a start-up stage, the epoxidation reaction conditions comprise trickle bed conditions.

In some preferred alternative embodiments of the process for preparing an olefin oxide comprising a normal run stage and a start-up stage, the epoxidation reaction conditions comprise fixed bed conditions.

Catalyst

In some preferred alternative embodiments of the process for preparing an olefin oxide comprising a normal run stage and a start-up stage, the heterogeneous epoxidation catalyst comprises a zeolitic material having a framework structure comprising Si, O and Ti.

In some preferred alternative embodiments of the process for preparing an olefin oxide comprising a normal run stage and a start-up stage, the zeolitic material comprises Ti in an amount in the range of from 0.2 to 5 weight-%, preferably in the range of from 0.5 to 4 weight-%, more preferably in the range of from 0.7 to 3 weight-%, calculated as elemental Ti and based on the total weight of the zeolitic material.

In some preferred alternative embodiments of the process for preparing an olefin oxide comprising a normal run stage and a start-up stage, the zeolitic material having a framework structure comprising Si, O and Ti comprised in the epoxidation catalyst is a titanium zeolite having ABW, ACO, AEI, AEL, AEN, AET, AFG, AFI, AFN, AFO, AFR, AFS, AFT, AFX, AFY, AHT, ANA, APC, APD, AST, ASV, ATN, ATO, ATS, ATT, ATV, AWO, AWW, BCT, BEA, BEC, BIK, BOG, BPH,

BRE, CAN, CAS, CDO, CFI, CGF, CGS, CHA, CHI, CLO, CON, CZP, DAC, DDR, DFO, DFT, DOH, DON, EAB, EDI, EMT, EPI, ERI, ESV, ETR, EUO, FAU, FER, FRA, GIS, GIU, GME, GON, GOO, HEU, IFR, ISV, ITE, ITH, ITQ, ITW, IWR, IWW, JBW, KFI, LAU, LEV, LIO, LOS, LOV, LTA, LTL, LTN, MAR, MAZ, MCM-22(S), MCM-36, MCM-56, MEI, MEL, MEP, MER, MIT-
5 1, MMFI, MFS, MON, MOR, MSE, MSO, MTF, MTN, MTT, MTW, MWW, NAB, NAT, NEES, NON, NPO, OBW, OFF, OSI, OSO, PAR, PAU, PHI, PON, RHO, RON, RRO, RSN, RTE, RTH, RUT, RWR, RWY, SAO, SAS, SAT, SAV, SBE, SBS, SBT, SFE, SFF, SFG, SFH, SFN SFO, SGT, SOD, SSY, STF, STI, STT, TER, THO, TON, TSC, UEI, UFI, UOZ, USI, UTL, VET, VFI, VNI, VSV, WEI, WEN, YUG, ZON SVR, SVY framework structure or a mixed structure of two or
10 more of these framework types; more preferably the zeolitic material having a framework structure comprising Si, O and Ti is a titanium zeolite having an MFI framework type, an MEL framework type, an MWW framework type, an MCM-22(S) framework type, an MCM-56 framework type, an IEZ-MWW framework type, an MCM-36 framework type, an ITQ framework type, a BEA framework type, a MOR framework type, or a mixed structure of two or more of these
15 framework types; more preferably the zeolitic material having a framework structure comprising Si, O and Ti is a titanium zeolite having an MFI framework type, or an MWW framework type; more preferably the zeolitic material having a framework structure comprising Si, O and Ti has framework type MFI; more preferably the zeolitic material having a framework structure comprising Si, O and Ti is a titanium silicalite-1 (TS-1).

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Preferably, the heterogeneous epoxidation catalyst further comprises a binder, which preferably comprises silicium dioxide.

Preferably, the heterogeneous epoxidation catalyst is in the form of a molding, preferably in the
25 form of a strand or a granule.

A strand has a cross section wherein the cross section preferably has a hexagonal, rectangular, quadratic, triangular, trilobe, oval, or circular shape. In some preferred embodiments, the molding has the form of a strand having a circular cross-section, which is more preferably formed by
30 extrusion (cylindrical extrudate). A granule preferably comprises particles having a form selected from cylinder, sphere, trilobe (particle having a trilobe cross section), and mixed forms of two or more of these forms, wherein the granule comprises particles of one form as well as mixtures of particles having two or more of these forms. A "sphere" comprises an ideal sphere form but also spheroidal forms. A "cylinder" comprises forms having a high h which is larger than the
35 radius of the circle area as well as forms having a high h which is smaller than the radius of the circle area (tablet form).

In some preferred alternative embodiments of the process for preparing an olefin oxide comprising a normal run stage and a start-up stage, from 95 to 100 weight-%, preferably from 98 to 100 weight-%, more preferably from 99 to 100 weight-%, more preferably from 99.5 to 100 weight-%, more preferably from 99.9 to 100 weight-% of the molding consist of the zeolitic material and the binder.

In some preferred alternative embodiments of the process for preparing an olefin oxide comprising a normal run stage and a start-up stage, from 95 to 100 weight-%, preferably from 98 to 100 weight-%, more preferably from 99 to 100 weight-%, more preferably from 99.5 to 100 weight-%, more preferably from 99.9 to 100 weight-% of the binder comprised in the molding consist of Si and O.

Preferably, the heterogeneous epoxidation catalyst, preferably the molding, comprises the binder, calculated as SiO_2 , in an amount in the range of from 1 to 95 weight-%, preferably in the range of from 3 to 70 weight-%, more preferably in the range of from 5 to 50 weight-%, more preferably in the range of from 10 to 30 weight-%, based on the total weight of the epoxidation catalyst, preferably based on the total weight of the molding and/or wherein the heterogeneous epoxidation catalyst, preferably the molding, comprises the zeolitic material in an amount in the range of from 5 to 99 weight-%, preferably in the range of from 30 to 97 weight-%, more preferably in the range of from 50 to 95 weight-%, more preferably in the range of from 70 to 90 weight-%, based on the total weight of the heterogeneous epoxidation catalyst, preferably based on the total weight of the molding.

Hydrogen peroxide

In some preferred alternative embodiments of the process for preparing an olefin oxide comprising a normal run stage and a start-up stage, the hydrogen peroxide is provided as aqueous hydrogen peroxide solution, which preferably has a total organic carbon content (TOC) in the range of from 100 to 800 mg per kg hydrogen peroxide comprised in the aqueous hydrogen peroxide solution, preferably in the range of from 120 to 750 mg per kg hydrogen peroxide comprised in the aqueous hydrogen peroxide solution, more preferably in the range of from 150 to 700 mg per kg hydrogen peroxide comprised in the aqueous hydrogen peroxide solution, determined according to DIN EN 1484 (April 2019). In some preferred alternative embodiments of the process for preparing an olefin oxide comprising a normal run stage and a start-up stage, the hydrogen peroxide has a pH in the range of from 0 to 3.0, preferably in the range of from 0.1 to 2.5, more preferably in the range of from 0.5 to 2.3, determined with a pH sensitive glass electrode according to CEFIC PEROXYGENS H₂O₂ AM-7160 standard (2003). In some preferred alternative embodiments of the process for preparing an olefin oxide comprising a normal run

stage and a start-up stage, the hydrogen peroxide comprises from 20 to 85 weight-%, preferably from 30 to 75 weight-%, more preferably from 40 to 70 weight-% of hydrogen peroxide, relative to the total weight of the aqueous hydrogen peroxide solution. In some preferred alternative embodiments of the process for preparing an olefin oxide comprising a normal run stage and a start-up stage, the hydrogen peroxide is obtained or obtainable from an anthraquinone process.

Solvent

In some preferred alternative embodiments of the process for preparing an olefin oxide comprising a normal run stage and a start-up stage, the organic solvent is an organic epoxidation solvent, preferably the organic solvent is selected from the group consisting of alcohol, acetonitrile, propionitrile and mixtures of two or more thereof; more preferably selected from the group consisting of alcohol, acetonitrile and mixtures of alcohol and acetonitrile; more preferably the organic solvent comprises at least an alcohol, wherein the alcohol is preferably a C1 to C5 mono alcohol or a mixture of two or more C1 to C5 alcohols, more preferably the alcohol comprises at least methanol, wherein the organic solvent more preferably comprises at least 90 weight-%, more preferably at least 95 weight-%, more preferably at least 98 weight-%, more preferably at least 99 weight-%, of methanol.

Olefin (oxide)

In some preferred alternative embodiments of the process for preparing an olefin oxide comprising a normal run stage and a start-up stage, the olefin is a C₂-C₁₀ alkene, preferably a C₂-C₅ alkene, more preferably a C₂-C₄ alkene, more preferably ethylene or propylene, more preferably propylene. The olefin oxide, especially the olefin oxide removed from the epoxidation zone with the effluent stream comprising olefin oxide, water and organic solvent in (C), is a C₂-C₁₀ alkene oxide, preferably a C₂-C₅ alkene oxide, more preferably a C₂-C₄ alkene oxide, more preferably ethylene oxide or propylene oxide, more preferably propylene oxide.

The disclosure above for the process of the second aspect equally applies for the steps such as (A), (B), (C) of the normal run stage and for the steps such as (a), (b) of the start-up stage.

3rd aspect – olefin oxide

In a third aspect, the invention is directed to an olefin oxide, preferably propylene oxide, obtained or obtainable from the process of the second aspect.

The present invention is further illustrated by the following embodiments and combinations of embodiments as indicated by the respective dependencies and back-references. In particular, it is noted that in each instance where a range of embodiments is mentioned, for example in the context of a term such as "The ... of any of embodiments 1 to 4", every embodiment in this

5 range is meant to be explicitly disclosed for the skilled person, i.e. the wording of this term is to be understood by the skilled person as being synonymous to "The ... of any of embodiments 1, 2, 3, and 4".

- 10 1. A start-up method for a process for preparing an olefin oxide comprising a normal run stage, wherein the normal run stage comprises providing olefin, hydrogen peroxide and organic solvent into an epoxidation zone comprising an heterogeneous epoxidation catalyst, so that a reaction mixture comprising olefin, hydrogen peroxide and organic solvent is formed and subjecting the reaction mixture to epoxidation reaction conditions in the epoxidation zone, thereby obtaining a mixture comprising olefin oxide and organic solvent;
- 15 wherein the start-up method comprises
 - (a) providing olefin and organic solvent for a first period of time P_1 to the epoxidation zone, so that a first mixture 1 is formed, which is essentially free of hydrogen peroxide, and contacting the first mixture 1 over P_1 under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst;
 - 20 (b) after the first period of time providing olefin, organic solvent and hydrogen peroxide to the epoxidation zone for a second period of time P_2 , so that a second mixture 2 is formed, which comprises olefin, organic solvent, and hydrogen peroxide, and contacting the second mixture 2 over P_2 under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst.
- 25 2. The start-up method of embodiment 1, wherein the amount of olefin provided in (a) is lower than the amount intended to be provided in the normal run stage.
- 30 3. The start-up method of embodiment 1 or 2, wherein the amounts of olefin and of hydrogen peroxide provided in (b) are lower than the respective amounts intended to be provided in the normal run stage, wherein preferably, the molar amount of olefin provided in (b) is higher than the molar amount of hydrogen peroxide provided in (b).
- 35 4. The start-up method of any one of embodiments 1 to 3, wherein (b) comprises
 - (b') after the first period of time P_1 , providing organic solvent and olefin and hydrogen peroxide in initial amounts to the epoxidation zone for a period of time P_2 , so that a mixture is formed, which comprises organic solvent, olefin, and hydrogen peroxide,

- wherein the amounts of the hydrogen peroxide and of the olefin are lower than the amounts intended to be provided in the normal run stage, and increasing the amount of the hydrogen peroxide and the amount of the olefin over the period of time P_2' up to the amounts intended to be provided in the normal run stage, so that a mixture 2' is formed, and contacting the mixture 2' over P_2' under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst; wherein preferably, the molar amount of olefin initially provided is higher than the molar amount of hydrogen peroxide initially provided and the molar amount of olefin provided during the increase is higher than the molar amount of hydrogen peroxide provided during the increase.
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5. The start-up method of any one of embodiments 1 to 4, wherein the olefin is provided in (a) in a molar ratio relative to the molar amount of hydrogen peroxide intended to be used in the normal run stage in the range of from 0.1:1 to 4:1, preferably in the range of from 0.1:1 to 1:1 or in the range of from 2:1 to 4:1.
 6. The start-up method of any one of embodiments 1 to 5, wherein the olefin and the hydrogen peroxide are provided in (b) or in (b') respectively so that the molar ratio of olefin : hydrogen peroxide in the second mixture 2 formed in (b) or in the mixture formed in (b') respectively is in the range of from 1.1:1 to 5:1, preferably in the range of from 1.1:1 to 2:1 or in the range of from 3:1 to 5:1.
 7. The start-up method of any one of embodiments 1 to 6, wherein (a) comprises
 - (a.1) providing olefin and organic solvent for a first period of time P_1 to the epoxidation zone, so that a first mixture 1 is formed, which is essentially free of hydrogen peroxide, and contacting the first mixture 1 over P_1 under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst;
 - (a.2) removing during P_1 an effluent stream from the epoxidation zone, the effluent stream comprising olefin and organic solvent.
 8. The start-up method of any one of embodiments 1 to 7, wherein (b) comprises
 - (b.1) after the first period of time providing olefin, organic solvent and hydrogen peroxide to the epoxidation zone for a second period of time P_2 , so that a second mixture 2 is formed, which comprises olefin, organic solvent, and hydrogen peroxide, and contacting the second mixture 2 over P_2 under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst;
 - (b.2) removing during the respective period of time an effluent stream from the epoxidation zone, the effluent stream comprising olefin oxide and organic solvent;

and/or wherein (b') comprises

(b'.1) after the first period of time P_1 , providing organic solvent and olefin and hydrogen peroxide in initial amounts to the epoxidation zone for a period of time P_2 , so that a mixture is formed, which comprises organic solvent, olefin, and hydrogen peroxide, wherein the amounts of the hydrogen peroxide and of the olefin are lower than the amounts intended to be provided in the normal run stage, and increasing the amount of the hydrogen peroxide and the amount of the olefin over the period of time P_2 up to the amounts intended to be provided in the normal run stage, so that a mixture 2' is formed, and contacting the mixture 2' over P_2 under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst;

(b'.2) removing during the respective period of time an effluent stream from the epoxidation zone, the effluent stream comprising olefin oxide and organic solvent.

9. The start-up method of any one of embodiments 1 to 8, wherein in any one of (a), (a.1), (b), (b'), (b.1), (b'.1), preferably in at least one of (b), (b'), (b.1), (b'.1), more preferably in each of (b), (b'), (b.1), (b'.1), an additive is provided to the epoxidation zone, wherein the additive is selected from the group consisting of potassium salt of an inorganic acid, potassium salt of an organic acid, ammonia, ammonium salt of an inorganic acid, ammonium salt of an organic acid and mixtures of two or more thereof;

wherein the additive is preferably selected from the group consisting of potassium dihydrogen phosphate, dipotassium hydrogen phosphate, potassium formate, potassium acetate, potassium hydrogen carbonate, dipotassium etidronate, ammonium dihydrogen phosphate, diammonium hydrogen phosphate, ammonia and mixtures of two or more thereof,

more preferably from the group consisting of potassium dihydrogen phosphate, dipotassium hydrogen phosphate, dipotassium etidronate, ammonia and mixtures of two or more thereof;

wherein the additive more preferably comprises at least dipotassium etidronate or dipotassium hydrogen phosphate or a mixture of dipotassium etidronate and dipotassium hydrogen phosphate, wherein more preferably in the range of from 95 to 100 weight-% of the additive are dipotassium etidronate or dipotassium hydrogen phosphate or a mixture of dipotassium etidronate and dipotassium hydrogen phosphate.

10. The start-up method of embodiment 10, wherein the additive is in case of ammonia provided in pure form or in aqueous solution, wherein the additive is in case of being selected

- from the group consisting of potassium salt of an inorganic acid, potassium salt of an organic acid, ammonium salt of an inorganic acid, ammonium salt of an organic acid or any mixture comprising two or more thereof or any mixture comprising ammonia and at least one thereof provided in aqueous solution;
- 5 wherein the additive in aqueous solution releases or forms one or more cation(s) M, wherein M represents in case of a potassium salt K^+ , or, in case of ammonia or ammonium salts, M represents the sum of NH_4^+ and NH_3 .
11. The start-up method of embodiment 9 or 10, wherein the additive is preferably pre-mixed
10 with the organic solvent or with the hydrogen peroxide, preferably with the organic solvent, prior to being provided to the epoxidation zone.
12. The start-up method of any one of embodiment 9 to 11, wherein the additive is provided in any one of (a), (b), (b'), (a.1), (b.1), (b'.1), preferably in at least in any one of (b), (b'),
15 (b.1), (b'.1), more preferably in each of (b), (b'), (b.1), (b'.1), in a molar ratio M : hydrogen peroxide in the range of from $1 \times 10^{-5} : 1$ to $1 \times 10^{-3} : 1$.
13. The start-up method of any one of embodiments 1 to 12, wherein the first period of time P_1 is preferably a period of time in the range of from 1 minutes to 5 hours, more preferably in
20 the range of from 5 minutes to 1 hour, more preferably in the range of from 10 minutes to 30 minutes; and/or wherein the second period of time P_2 or P_2' respectively is preferably a period of time in the range of from 30 minutes to 24 hours, more preferably in the range of from 2 to 18 hours, more preferably in the range of from 4 to 12 hours.
25
14. The start-up method of any one of embodiments 1 to 13 further comprising before (a)
(x) providing an organic solvent stream for a period of time P_x to the epoxidation zone, wherein P_x is preferably a period of time in the range of from 10 minutes to 24 hours.
- 30 15. The start-up method of any one of embodiments 1 to 14, which is carried out continuously.
16. The start-up method of any one of embodiments 1 to 15, wherein the contacting under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst is carried out at an absolute pressure in the epoxidation zone in the range of
35 from 0.5 to 5.0 MPa, preferably in the range of from 1.5 to 3.0 MPa, more preferably in the range of from 1.8 to 2.8 MPa.

17. The start-up method of any one of embodiments 1 to 16, wherein the contacting under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst is carried out at a temperature in the epoxidation zone in the range of from 20 to 75 °C, preferably in the range of from 22 to 75 °C, more preferably in the range of from 24 to 70 °C, more preferably in the range of from 25 to 65 °C.
18. The start-up method of any one of embodiments 1 to 17, wherein the epoxidation reaction conditions comprise trickle bed conditions.
19. The start-up method of any one of embodiments 1 to 17, wherein the epoxidation reaction conditions comprise fixed bed conditions.
20. The start-up method of any one of embodiments 1 to 19, wherein the heterogeneous epoxidation catalyst comprises a zeolitic material having a framework structure comprising Si, O and Ti.
21. The start-up method of embodiment 20, wherein the zeolitic material comprises Ti in an amount in the range of from 0.2 to 5 weight-%, preferably in the range of from 0.5 to 4 weight-%, more preferably in the range of from 0.7 to 3 weight-%, calculated as elemental Ti and based on the total weight of the zeolitic material.
22. The start-up method of embodiment 20 or 21, wherein the zeolitic material having a framework structure comprising Si, O and Ti comprised in the epoxidation catalyst is a titanium zeolite having ABW, ACO, AEI, AEL, AEN, AET, AFG, AFI, AFN, AFO, AFR, AFS, AFT, AFX, AFY, AHT, ANA, APC, APD, AST, ASV, ATN, ATO, ATS, ATT, ATV, AWO, AWW, BCT, BEA, BEC, BIK, BOG, BPH, BRE, CAN, CAS, CDO, CFI, CGF, CGS, CHA, CHI, CLO, CON, CZP, DAC, DDR, DFO, DFT, DOH, DON, EAB, EDI, EMT, EPI, ERI, ESV, ETR, EUO, FAU, FER, FRA, GIS, GIU, GME, GON, GOO, HEU, IFR, ISV, ITE, ITH, ITQ, ITW, IWR, IWW, JBW, KFI, LAU, LEV, LIO, LOS, LOV, LTA, LTL, LTN, MAR, MAZ, MCM-22(S), MCM-36, MCM-56, MEI, MEL, MEP, MER, MIT-1, MMFI, MFS, MON, MOR, MSE, MSO, MTF, MTN, MTT, MTW, MWW, NAB, NAT, NEES, NON, NPO, OBW, OFF, OSI, OSO, PAR, PAU, PHI, PON, RHO, RON, RRO, RSN, RTE, RTH, RUT, RWR, RWY, SAO, SAS, SAT, SAV, SBE, SBS, SBT, SFE, SFF, SFG, SFH, SFN, SFO, SGT, SOD, SSV, STF, STI, STT, TER, THO, TON, TSC, UEI, UFI, UOZ, USI, UTL, VET, VFI, VNI, VSV, WEI, WEN, YUG, ZON SVR, SVY framework structure or a mixed structure of two or more of these framework types; more preferably the zeolitic material having a framework structure comprising Si, O and Ti is a titanium zeolite having an MFI framework type, an MEL framework type, an MWW framework type, an MCM-22(S) framework type, an

- MCM-56 framework type, an IEZ-MWW framework type, an MCM-36 framework type, an ITQ framework type, a BEA framework type, a MOR framework type, or a mixed structure of two or more of these framework types; more preferably the zeolitic material having a framework structure comprising Si, O and Ti is a titanium zeolite having an MFI framework type, or an MWW framework type; more preferably the zeolitic material having a framework structure comprising Si, O and Ti has framework type MFI; more preferably the zeolitic material having a framework structure comprising Si, O and Ti is a titanium silicalite-1 (TS-1).
23. The start-up method of any one of embodiments 20 to 22, wherein the heterogeneous epoxidation catalyst further comprises a binder, which preferably comprises silicium dioxide.
24. The start-up method of embodiment 23, wherein the heterogeneous epoxidation catalyst is in the form of a molding, preferably in the form of a strand or a granule.
25. The start-up method of embodiment 23 or 24, wherein from 95 to 100 weight-%, preferably from 98 to 100 weight-%, more preferably from 99 to 100 weight-%, more preferably from 99.5 to 100 weight-%, more preferably from 99.9 to 100 weight-% of the molding consist of the zeolitic material and the binder.
26. The start-up method of any one of embodiments 23 to 25, wherein from 95 to 100 weight-%, preferably from 98 to 100 weight-%, more preferably from 99 to 100 weight-%, more preferably from 99.5 to 100 weight-%, more preferably from 99.9 to 100 weight-% of the binder comprised in the molding consist of Si and O.
27. The start-up method of embodiment 26, wherein the heterogeneous epoxidation catalyst, preferably the molding, comprises the binder, calculated as SiO_2 , in an amount in the range of from 1 to 95 weight-%, preferably in the range of from 3 to 70 weight-%, more preferably in the range of from 5 to 50 weight-%, more preferably in the range of from 10 to 30 weight-%, based on the total weight of the epoxidation catalyst, preferably based on the total weight of the molding and/or wherein the heterogeneous epoxidation catalyst, preferably the molding, comprises the zeolitic material in an amount in the range of from 5 to 99 weight-%, preferably in the range of from 30 to 97 weight-%, more preferably in the range of from 50 to 95 weight-%, more preferably in the range of from 70 to 90 weight-%, based on the total weight of the heterogeneous epoxidation catalyst, preferably based on the total weight of the molding.

28. The start-up method of any one of embodiments 1 to 27, wherein the hydrogen peroxide is provided as aqueous hydrogen peroxide solution, which preferably has a total organic carbon content (TOC) in the range of from 100 to 800 mg per kg hydrogen peroxide comprised in the aqueous hydrogen peroxide solution, preferably in the range of from 120 to 750 mg per kg hydrogen peroxide comprised in the aqueous hydrogen peroxide solution, more preferably in the range of from 150 to 700 mg per kg hydrogen peroxide comprised in the aqueous hydrogen peroxide solution, determined according to DIN EN 1484 (April 2019).
29. The start-up method of any one of embodiments 1 to 28, wherein the hydrogen peroxide has a pH in the range of from 0 to 3.0, preferably in the range of from 0.1 to 2.5, more preferably in the range of from 0.5 to 2.3, determined with a pH sensitive glass electrode according to CEFIC PEROXYGENS H₂O₂ AM-7160 standard (2003).
30. The start-up method of any one of embodiments 1 to 29, wherein the hydrogen peroxide comprises from 20 to 85 weight-%, preferably from 30 to 75 weight-%, more preferably from 40 to 70 weight-% of hydrogen peroxide, relative to the total weight of the aqueous hydrogen peroxide solution.
31. The start-up method of any one of embodiments 1 to 30, wherein the hydrogen peroxide is obtained or obtainable from an anthraquinone process.
32. The start-up method of any one of embodiments 1 to 31, wherein the organic solvent is an organic epoxidation solvent, preferably the organic solvent is selected from the group consisting of alcohol, acetonitrile, propionitrile and mixtures of two or more thereof; more preferably selected from the group consisting of alcohol, acetonitrile and mixtures of alcohol and acetonitrile; more preferably the organic solvent comprises at least an alcohol, wherein the alcohol is preferably a C₁ to C₅ mono alcohol or a mixture of two or more C₁ to C₅ alcohols, more preferably the alcohol comprises at least methanol, wherein the organic solvent more preferably comprises at least 90 weight-%, more preferably at least 95 weight-%, more preferably at least 98 weight-%, more preferably at least 99 weight-%, of methanol.
33. The start-up method of any one of embodiments 1 to 33, wherein the olefin is a C₂-C₁₀ alkene, preferably a C₂-C₅ alkene, more preferably a C₂-C₄ alkene, more preferably ethylene or propylene, more preferably propylene.

34. A process for preparing an olefin oxide comprising a normal run stage and a start-up stage, wherein the normal run stage comprises
- (A) providing olefin, hydrogen peroxide, water and organic solvent into an epoxidation zone comprising a heterogeneous epoxidation catalyst, so that a reaction mixture comprising olefin, hydrogen peroxide, water and organic solvent is formed;
 - (B) subjecting the reaction mixture from (A) to epoxidation reaction conditions in the epoxidation zone, thereby obtaining a mixture comprising olefin oxide, water and organic solvent;
 - (C) removing an effluent stream from the epoxidation zone, comprising olefin oxide, water and organic solvent;
- wherein the start-up stage comprises
- (a) providing olefin and organic solvent for a first period of time P_1 to the epoxidation zone, so that a first mixture 1 is formed, which is essentially free of hydrogen peroxide, and contacting the first mixture 1 over P_1 under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst;
 - (b) after the first period of time providing organic solvent, olefin and hydrogen peroxide to the epoxidation zone for a second period of time P_2 , so that a second mixture 2 is formed, which comprises olefin, organic solvent, and hydrogen peroxide, and contacting the second mixture 2 over P_2 under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst.
35. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of embodiment 34, wherein the amount of olefin provided in (a) is lower than the amount intended to be provided in the normal run stage.
36. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of embodiment 34 or 35, wherein the amounts of olefin and of hydrogen peroxide provided in (b) are lower than the respective amounts intended to be provided in the normal run stage, wherein preferably, the molar amount of olefin provided in (b) is higher than the molar amount of hydrogen peroxide provided in (b).
37. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of any one of embodiments 34 to 36, wherein (b) comprises
- (b') after the first period of time P_1 , providing organic solvent and olefin and hydrogen peroxide in initial amounts to the epoxidation zone for a period of time P_2 , so that a mixture is formed, which comprises organic solvent, olefin, and hydrogen peroxide, wherein the amounts of the hydrogen peroxide and of the olefin are lower than the amounts intended to be provided in the normal run stage, and

- increasing the amount of the hydrogen peroxide and the amount of the olefin over the period of time P_2 up to the amounts intended to be provided in the normal run stage, so that a mixture 2' is formed, and contacting the mixture 2' over P_2 under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst; wherein preferably, the molar amount of olefin initially provided is higher than the molar amount of hydrogen peroxide initially provided and the molar amount of olefin provided during the increase is higher than the molar amount of hydrogen peroxide provided during the increase.
38. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of any one of embodiments 34 to 37, wherein the olefin is provided in (a) in a molar ratio relative to the molar amount of hydrogen peroxide intended to be used in the normal run stage in the range of from 0.1:1 to 4:1, preferably in the range of from 0.1:1 to 1:1 or in the range of from 2:1 to 4:1.
39. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of any one of embodiments 34 to 38, wherein the olefin and the hydrogen peroxide are provided in (b) or in (b') respectively so that the molar ratio of olefin : hydrogen peroxide in the second mixture 2 formed in (b) or in the mixture formed in (b') respectively is in the range of from 1.1:1 to 5:1, preferably in the range of from 1.1:1 to 2:1 or in the range of from 3:1 to 5:1.
40. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of any one of embodiments 34 to 39, wherein (a) comprises
- (a.1) providing olefin and organic solvent for a first period of time P_1 to the epoxidation zone, so that a first mixture 1 is formed, which is essentially free of hydrogen peroxide, and contacting the first mixture 1 over P_1 under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst;
- (a.2) removing during P_1 an effluent stream from the epoxidation zone, the effluent stream comprising olefin and organic solvent.
41. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of any one of embodiments 34 to 40, wherein (b) comprises
- (b.1) after the first period of time providing olefin, organic solvent and hydrogen peroxide to the epoxidation zone for a second period of time P_2 , so that a second mixture 2 is formed, which comprises olefin, organic solvent, and hydrogen peroxide, and contacting the second mixture 2 over P_2 under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst;

- (b.2) removing during the respective period of time an effluent stream from the epoxidation zone, the effluent stream comprising olefin oxide and organic solvent;
and/or wherein (b') comprises
- (b'.1) after the first period of time P_1 , providing organic solvent and olefin and hydrogen peroxide in initial amounts to the epoxidation zone for a period of time P_2 , so that a mixture is formed, which comprises organic solvent, olefin, and hydrogen peroxide, wherein the amounts of the hydrogen peroxide and of the olefin are lower than the amounts intended to be provided in the normal run stage, and increasing the amount of the hydrogen peroxide and the amount of the olefin over the period of time P_2 up to the amounts intended to be provided in the normal run stage, so that a mixture 2' is formed, and contacting the mixture 2' over P_2 under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst;
- (b'.2) removing during the respective period of time an effluent stream from the epoxidation zone, the effluent stream comprising olefin oxide and organic solvent.
42. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of any one of embodiments 34 to 41, wherein in any one of (a), (a.1), (b), (b'), (b.1), (b'.1), preferably in at least one of (b), (b'), (b.1), (b'.1), more preferably in each of (b), (b'), (b.1), (b'.1), an additive is provided to the epoxidation zone, wherein the additive is selected from the group consisting of potassium salt of an inorganic acid, potassium salt of an organic acid, ammonia, ammonium salt of an inorganic acid, ammonium salt of an organic acid and mixtures of two or more thereof;
- wherein the additive is preferably selected from the group consisting of potassium dihydrogen phosphate, dipotassium hydrogen phosphate, potassium formate, potassium acetate, potassium hydrogen carbonate, dipotassium etidronate, ammonium dihydrogen phosphate, diammonium hydrogen phosphate, ammonia and mixtures of two or more thereof;
- more preferably from the group consisting of potassium dihydrogen phosphate, dipotassium hydrogen phosphate, dipotassium etidronate, ammonia and mixtures of two or more thereof;
- wherein the additive more preferably comprises at least dipotassium etidronate or dipotassium hydrogen phosphate or a mixture of dipotassium etidronate and dipotassium hydrogen phosphate, wherein more preferably in the range of from 95 to 100 weight-% of the additive are dipotassium etidronate or dipotassium hydrogen phosphate or a mixture of dipotassium etidronate and dipotassium hydrogen phosphate.

43. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of embodiment 42, wherein the additive is in case of ammonia provided in pure form or in aqueous solution, wherein the additive is in case of being selected from the group consisting of potassium salt of an inorganic acid, potassium salt of an organic acid, ammonium salt of an inorganic acid, ammonium salt of an organic acid or any mixture comprising two or more thereof or any mixture comprising ammonia and at least one thereof provided in aqueous solution;
5 wherein the additive in aqueous solution releases or forms one or more cation(s) M, wherein M represents in case of a potassium salt K^+ , or, in case of ammonia or ammonium salts, M represents the sum of NH_4^+ and NH_3 .
10
44. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of embodiment 42 or 43, wherein the additive is preferably pre-mixed with the organic solvent or with the hydrogen peroxide, preferably with the organic solvent, prior to being provided to the epoxidation zone.
15
45. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of any one of embodiments 42 to 44, wherein the additive is provided in any one of (a), (b), (b'), (a.1), (b.1), (b'.1), preferably in at least in any one of (b), (b'), (b.1), (b'.1), more preferably in each of (b), (b'), (b.1), (b'.1), in a molar ratio M : hydrogen peroxide in the range of from 1×10^{-5} : 1 to 1×10^{-3} : 1.
20
46. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of any one of embodiments 34 to 45, wherein the first period of time P_1 is preferably a period of time in the range of from 1 minutes to 5 hours, more preferably in the range of from 5 minutes to 1 hour, more preferably in the range of from 10 minutes to 30 minutes; and/or
25 wherein the second period of time P_2 or P_2' respectively is preferably a period of time in the range of from 30 minutes to 24 hours, more preferably in the range of from 2 to 18 hours, more preferably in the range of from 4 to 12 hours.
30
47. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of any one of embodiments 34 to 46, further comprising before (a)
35 (x) providing an organic solvent stream for a period of time P_x to the epoxidation zone, wherein P_x is preferably a period of time in the range of from 10 minutes to 24 hours.

48. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of any one of embodiments 34 to 41, which is carried out continuously.
49. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of any one of embodiments 34 to 48, wherein the contacting under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst is carried out at an absolute pressure in the epoxidation zone in the range of from 0.5 to 5.0 MPa, preferably in the range of from 1.5 to 3.0 MPa, more preferably in the range of from 1.8 to 2.8 MPa.
50. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of any one of embodiments 34 to 49, wherein the contacting under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst is carried out at a temperature in the epoxidation zone in the range of from 20 to 75 °C, preferably in the range of from 22 to 75 °C, more preferably in the range of from 24 to 70 °C, more preferably in the range of from 25 to 65 °C.
51. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of any one of embodiments 34 to 50, wherein the epoxidation reaction conditions comprise trickle bed conditions.
52. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of any one of embodiments 34 to 51, wherein the epoxidation reaction conditions comprise fixed bed conditions.
53. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of any one of embodiments 34 to 52, wherein the heterogeneous epoxidation catalyst comprises a zeolitic material having a framework structure comprising Si, O and Ti.
54. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of embodiment 53, wherein the zeolitic material comprises Ti in an amount in the range of from 0.2 to 5 weight-%, preferably in the range of from 0.5 to 4 weight-%, more preferably in the range of from 0.7 to 3 weight-%, calculated as elemental Ti and based on the total weight of the zeolitic material.
55. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of embodiment 53 or 54, wherein the zeolitic material having a framework structure comprising Si, O and Ti comprised in the epoxidation catalyst is a titanium zeolite having

- ABW, ACO, AEI, AEL, AEN, AET, AFG, AFI, AFN, AFO, AFR, AFS, AFT, AFX, AFY, AHT, ANA, APC, APD, AST, ASV, ATN, ATO, ATS, ATT, ATV, AWO, AWW, BCT, BEA, BEC, BIK, BOG, BPH, BRE, CAN, CAS, CDO, CFI, CGF, CGS, CHA, CHI, CLO, CON, CZP, DAC, DDR, DFO, DFT, DOH, DON, EAB, EDI, EMT, EPI, ERI, ESV, ETR, EUO, FAU, FER, FRA, GIS, GIU, GME, GON, GOO, HEU, IFR, ISV, ITE, ITH, ITQ, ITW, IWR, IWW, JBW, KFI, LAU, LEV, LIO, LOS, LOV, LTA, LTL, LTN, MAR, MAZ, MCM-22(S), MCM-36, MCM-56, MEI, MEL, MEP, MER, MIT-1, MMFI, MFS, MON, MOR, MSE, MSO, MTF, MTN, MTT, MTW, MWW, NAB, NAT, NEES, NON, NPO, OBW, OFF, OSI, OSO, PAR, PAU, PHI, PON, RHO, RON, RRO, RSN, RTE, RTH, RUT, RWR, RWY, SAO, SAS, SAT, SAV, SBE, SBS, SBT, SFE, SFF, SFG, SFH, SFN SFO, SGT, SOD, SSY, STF, STI, STT, TER, THO, TON, TSC, UEI, UFI, UOZ, USI, UTL, VET, VFI, VNI, VSV, WEI, WEN, YUG, ZON SVR, SVY framework structure or a mixed structure of two or more of these framework types; more preferably the zeolitic material having a framework structure comprising Si, O and Ti is a titanium zeolite having an MFI framework type, an MEL framework type, an MWW framework type, an MCM-22(S) framework type, an MCM-56 framework type, an IEZ-MWW framework type, an MCM-36 framework type, an ITQ framework type, a BEA framework type, a MOR framework type, or a mixed structure of two or more of these framework types; more preferably the zeolitic material having a framework structure comprising Si, O and Ti is a titanium zeolite having an MFI framework type, or an MWW framework type; more preferably the zeolitic material having a framework structure comprising Si, O and Ti has framework type MFI; more preferably the zeolitic material having a framework structure comprising Si, O and Ti is a titanium silicalite-1 (TS-1).
56. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of any one of embodiments 53 to 55, wherein the heterogeneous epoxidation catalyst further comprises a binder, which preferably comprises silicium dioxide.
57. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of embodiment 56, wherein the heterogeneous epoxidation catalyst is in the form of a molding, preferably in the form of a strand or a granule.
58. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of embodiment 56 or 57, wherein from 95 to 100 weight-%, preferably from 98 to 100 weight-%, more preferably from 99 to 100 weight-%, more preferably from 99.5 to 100 weight-%, more preferably from 99.9 to 100 weight-% of the molding consist of the zeolitic material and the binder.

59. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of any one of embodiments 56 to 58, wherein from 95 to 100 weight-%, preferably from 98 to 100 weight-%, more preferably from 99 to 100 weight-%, more preferably from 99.5 to 100 weight-%, more preferably from 99.9 to 100 weight-% of the binder comprised in the molding consist of Si and O.
60. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of embodiment 59, wherein the heterogeneous epoxidation catalyst, preferably the molding, comprises the binder, calculated as SiO_2 , in an amount in the range of from 1 to 95 weight-%, preferably in the range of from 3 to 70 weight-%, more preferably in the range of from 5 to 50 weight-%, more preferably in the range of from 10 to 30 weight-%,, based on the total weight of the epoxidation catalyst, preferably based on the total weight of the molding and/or wherein the heterogeneous epoxidation catalyst, preferably the molding, comprises the zeolitic material in an amount in the range of from 5 to 99 weight-%, preferably in the range of from 30 to 97 weight-%, more preferably in the in the range of from 50 to 95 weight-%, more preferably in the range of from 70 to 90 weight-%, , based on the total weight of the heterogeneous epoxidation catalyst, preferably based on the total weight of the molding.
61. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of any one of embodiments 34 to 60, wherein the hydrogen peroxide is provided as aqueous hydrogen peroxide solution, which preferably has a total organic carbon content (TOC) in the range of from 100 to 800 mg per kg hydrogen peroxide comprised in the aqueous hydrogen peroxide solution, preferably in the range of from 120 to 750 mg per kg hydrogen peroxide comprised in the aqueous hydrogen peroxide solution, more preferably in the range of from 150 to 700 mg per kg hydrogen peroxide comprised in the aqueous hydrogen peroxide solution, determined according to DIN EN 1484 (April 2019).
62. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of any one of embodiments 34 to 61, wherein the hydrogen peroxide has a pH in the range of from 0 to 3.0, preferably in the range of from 0.1 to 2.5, more preferably in the range of from 0.5 to 2.3, determined with a pH sensitive glass electrode according to CEFIC PEROXYGENS H₂O₂ AM-7160 standard (2003).
63. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of any one of embodiments 34 to 62, wherein the hydrogen peroxide comprises from 20 to 85 weight-%, preferably from 30 to 75 weight-%, more preferably from 40 to

70 weight-% of hydrogen peroxide, relative to the total weight of the aqueous hydrogen peroxide solution.

64. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of any one of embodiments 34 to 63, wherein the hydrogen peroxide is obtained or obtainable from an anthraquinone process.
65. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of any one of embodiments 34 to 64, wherein the organic solvent is an organic epoxidation solvent, preferably the organic solvent is selected from the group consisting of alcohol, acetonitrile, propionitrile and mixtures of two or more thereof; more preferably selected from the group consisting of alcohol, acetonitrile and mixtures of alcohol and acetonitrile; more preferably the organic solvent comprises at least an alcohol, wherein the alcohol is preferably a C₁ to C₅ mono alcohol or a mixture of two or more C₁ to C₅ alcohols, more preferably the alcohol comprises at least methanol, wherein the organic solvent more preferably comprises at least 90 weight-%, more preferably at least 95 weight-%, more preferably at least 98 weight-%, more preferably at least 99 weight-%, of methanol.
66. The process for preparing an olefin oxide comprising a normal run stage and a start-up stage of any one of embodiments 34 to 65, wherein the olefin is a C₂-C₁₀ alkene, preferably a C₂-C₅ alkene, more preferably a C₂-C₄ alkene, more preferably ethylene or propylene, more preferably propylene.
67. The process for preparing an olefin oxide according to any one of embodiments 34 to 66, wherein the epoxidation in (B) is carried out at an absolute pressure in the reaction zones in the range of from 0.5 to 5.0 MPa, preferably in the range of from 1.5 to 3.0 MPa, more preferably in the range of from 1.8 to 2.8 MPa.
68. The process for preparing an olefin oxide according to any one of embodiments 34 to 67, wherein the epoxidation in (B) is carried out at a temperature in the reaction zones in the range of from 20 to 75°C, preferably in the range of from 25 to 75 °C, more preferably in the range of from 28 to 70 °C, more preferably in the range of from 30 to 65 °C.
69. The process for preparing an olefin oxide according to any one of embodiments 34 to 68, wherein the molar ratio of olefin : hydrogen peroxide (w/w) in the reaction mixture formed in (A) is in the range of from 1.1:1 to 5:1, preferably in the range of from 1.1:1 to 2:1 or in the range of from 3:1 to 5:1.

70. The process for preparing an olefin oxide according to any one of embodiments 34 to 69, wherein the weight ratio of organic solvent : hydrogen peroxide (w/w) in the reaction mixture formed in (A) is in the range of from 15:1 to 5:1, preferably in the range of from 12:1 to 6:1, more preferably in the range of from 12:1 to 8.5:1 or in the range of from 8:1 to 6:1.
71. The process for preparing an olefin oxide according to any one of embodiments 34 to 70, wherein the weight ratio of organic solvent : olefin (w/w) in the reaction mixture formed in (A) is in the range of from 10:1 to 1:0.1, preferably in the range of from 9:1 to 1:1, more preferably in the range of from 7:1 to 4:1 or in the range of from 1.5:1 to 1:1.
72. The process for preparing an olefin oxide according to any one of embodiments 34 to 71, wherein an additive is provided in (A), wherein the additive is selected from the group consisting of potassium salt of an inorganic acid, potassium salt of an organic acid, ammonia, ammonium salt of an inorganic acid, ammonium salt of an organic acid and mixtures of two or more thereof;
- wherein the additive is preferably selected from the group consisting of potassium dihydrogen phosphate, dipotassium hydrogen phosphate, potassium formate, potassium acetate, potassium hydrogen carbonate, dipotassium etidronate, ammonium dihydrogen phosphate, diammonium hydrogen phosphate, ammonia and mixtures of two or more thereof,
- more preferably from the group consisting of potassium dihydrogen phosphate, dipotassium hydrogen phosphate, dipotassium etidronate, ammonia and mixtures of two or more thereof;
- wherein the additive more preferably comprises at least dipotassium etidronate or dipotassium hydrogen phosphate or a mixture of dipotassium etidronate and dipotassium hydrogen phosphate, wherein more preferably in the range of from 95 to 100 weight-% of the additive are dipotassium etidronate.
73. The process for preparing an olefin oxide according to embodiment 72, wherein the additive is in case of ammonia provided in pure form or in aqueous solution, wherein the additive is in case of being selected from the group consisting of potassium salt of an inorganic acid, potassium salt of an organic acid, ammonium salt of an inorganic acid, ammonium salt of an organic acid or any mixture comprising two or more thereof or any mixture comprising ammonia and at least one thereof provided in aqueous solution;

wherein the additive in aqueous solution releases or forms one or more cation(s) M, wherein M represents in case of a potassium salt K⁺, or, in case of ammonia or ammonium salts, M represents the sum of NH₄⁺ and NH₃.

- 5
74.
- The process for preparing an olefin oxide according to embodiment 72 or 73, wherein the aqueous solution of additive comprises in the range of from 0.01 to 5 weight-%, preferably in the range of from 0.5 to 3 weight-%, more preferably in the range of from 1 to 2 weight-%, of additive, based on the overall weight of the aqueous solution.
- 10
75.
- The process for preparing an olefin oxide according to any one of embodiments 72 to 74, wherein the additive is preferably pre-mixed with the organic solvent or with the hydrogen peroxide, more preferably pre-mixed with the organic solvent, before being provided to the epoxidation zone in (A).
- 15
76.
- The process for preparing an olefin oxide according to any one of embodiments 34 to 75, wherein the additive is provided in (A) in a molar ratio M : hydrogen peroxide in the range of from 1 x 10⁻⁵ : 1 to 1 x 10⁻³ : 1.
- 20
77.
- The process for preparing an olefin oxide according to any one of embodiments 34 to 76, wherein the epoxidation reaction conditions according to (B) comprise fixed bed conditions.
- 25
78.
- The process for preparing an olefin oxide according to any one of embodiments 34 to 76, wherein the epoxidation reaction conditions according to (B) comprise trickle bed conditions.
79.
- Olefin oxide, preferably propylene oxide, obtained or obtainable from the process of any one of embodiments 34 to 78.
- 30
- The present invention is further illustrated by the following reference examples, comparative examples, and examples.

Examples

Chemicals	
Methanol	CH ₃ OH
Propylene	C ₃ H ₆ (C ₃)
Oxygen	O ₂

Nitrogen	N ₂
Hydrogen peroxide	H ₂ O ₂
Dipotassium hydrogen phosphate	K ₂ HPO ₄
Colloidal silica 40 weight-% in water	Ludox® AS-40
Titanium silicalite-1 zeolite	TS-1

The TS-1 catalyst was prepared according to Reference Example 2 of WO 2022/263437 A1 and was used in the form of extruded strands having a diameter of 1.5 mm (circular cross section). The extrudates contained 75 wt.-% of TS-1 and 25 wt.-% of silicon dioxide (from Ludox®).

5

Analytic methods

Determination of organic constituents

- 10 The concentration of the constituents of the effluent (product) stream coming from the 2nd separator (see Reference Example 1) was analyzed by Gas Chromatography (GC)

Determination of oxygen and nitrogen concentration

- 15 The flow of the vent stream after 2nd separator (see Reference Example 1) was measured by using a Brunkhorst flowmeter and the oxygen concentration was measured by using a Dräger Polytron 7000 detector with electrochemical sensor.

Determination of water concentration

20

Water concentration was determined by Karl Fischer titration.

Determination of hydrogen peroxide

- 25 Hydrogen peroxide was photometrically determined according to DIN38409, part 15 (June 1897).

Determination of total peroxides

- 30 Total peroxides (organic ROOH and H₂O₂) were given as the active oxygen content. The active oxygen content in the samples was determined by iodometry. The following gives a general description on how the determination was performed.

Approximately 5 g of the sample, weighed to the nearest 0.1 mg, were placed in a reaction vial, flushed with argon, and 40 ml of a 1:1 acetic acid / chloroform mixture were added to dissolve the sample. The reaction vial was provided with a cooler and placed in a stirring heating block, that was already preheated to 80°C. A weak argon flow was passed through the cooler to prevent the ingress of air. After the temperature had equilibrated, 5.0 ml of a saturated potassium iodide solution (about 60.0 g potassium iodide dissolved in 100 ml deionized water) were added through the cooler and the mixture was boiled under reflux for 10 min. In the next step, 40.0 ml deionized water were added, and the sample solution was titrated with a 0.01 M thiosulfate solution while using a platinum electrode as end point indicator.

Calculation of hydrogen peroxide conversion

The H₂O₂ conversion in % was calculated according to the following equation (I):

$$\text{H}_2\text{O}_2 \text{ conversion [\%]} = [(\text{mmol hydrogen peroxide}(\text{feed}) - \text{mmol hydrogen peroxide}(\text{effluent})) / \text{mmol hydrogen peroxide}(\text{feed})] * 100 \% \quad (\text{I})$$

, wherein “mmol hydrogen peroxide(feed)” means the mmol amount of H₂O₂ in the feed stream to the reactor and “mmol hydrogen peroxide(effluent)” means the mmol amount of H₂O₂ in the effluent stream coming out of the reactor.

Calculation of selectivities

The selectivity of a compound X in mol-% was calculated based on the following equation (II):

$$\text{Compound X [\%]} = (\text{mmol compound X}(\text{effluent}) \text{ per hour} / \text{mmol total}(\text{effluent}) \text{ per hour}) * 100 \% \quad (\text{II})$$

wherein X is a compound selected from PO, AA, PM-2, PM-1, acetol, MPG and ROOH, “mmol compound X(effluent)” means the mmol amount of said compound in the effluent stream coming out of the reactor and “mmol total(effluent)” means the sum of the mmol amount of propylene (C₃) converted into PO + AA + PM-2 + PM-1 + acetol + MPG + ROOH in the effluent stream coming out of the reactor per hour.

Reference Example 1: Experimental Reactor Setup for Example 1 and Comparative Example 1

- 140 g TS-1 catalyst were loaded into a reaction tube of a mini-plant with a length of 180 cm and a volume of 300 ml. The tube diameter was 0.75 inch (1.905 cm), with a wall thickness of 0.07 inch (0.19 cm). In the center of the reaction tube a smaller (0.125 inch (0.3175 cm)) tube was installed, containing thermoelements for measuring the temperature over the catalyst bed.
- 5 The hotspot, i.e. the zone where maximum reaction takes place, is typically located in the first half of a catalyst bed and preferably the majority of the thermoelements used is located in the first half of the catalyst bed.

- Propylene was stored in 50 l gas bottles, containing dip tubes, facilitating the transfer to the mini-plant by means of 25 bar nitrogen pressure. The precise amount was measured using a Brunkhorst flow meter with a 0-500 g/h range and the flow was controlled by means of a Flows-erve control-valve. Hydrogen peroxide was transferred into the reactor using a Grundfos pump DME2. The amount was determined using a balance. The measurement showed liters/minute. The respective additive solution was fed to the reactor, using a hydrogen peroxide LC pump.
- 15 The precise amount was determined using a balance. For feeding the methanol a Lewa pump with a range of 0 - 1500 ml/h was used. Feed control was accomplished using a Lewa KMM. Nitrogen was fed using a Flowserve control-valve. The amount was measured using a Brunkhorst flow meter with a range of 0-200 NI/h. "NI/h" means norm liter per hour, wherein 1 norm liter is the amount of gas, which fills 1 liter at 0°C and 1013 mbar (see DIN 1343 from January 1990).

- 20 Reactants, solvents, additive as indicated in detail in Example 1 and Comparative Example 1, all entered the reaction tube via a static mixer [0.25 inch (0.635 cm)-mixer], so that a combined feed stream was formed and fed to the reaction tube, wherein the feed direction was from the bottom to the top direction of the reaction tube.

- 25 The reactor effluent was passed through a 2 micrometer filter to remove fine (catalyst) particles before it was passed into the first separator. The bottom level valve controlled a level of 25 % in the first separator, while the upper pressure valve set a pressure of 20 bars over the entire up-stream reaction system. The second separator was also operated at a liquid level of 25 %, while
- 30 the upper pressure valve reduced the pressure to 2 bars. This lower pressure served for allowing the flashing of unconverted propylene, allowing a safe sample taking and having an additional safety buffer. The two separators had a volume of 2 liters each and were kept at a temperature of 5 °C, using cooling water. A nitrogen stream of a gas flow of 5 NI/h was fed through the entire system (reactor->1st separator->2nd separator->vent-system) to maintain a sufficient
- 35 gas flow in the direction of the vent to ascertain that traces of oxygen, formed by partial decomposition of H₂O₂, were flashed out and could be analyzed at the end of the vent pipe. A flowmeter was installed in the vent line, through which the gaseous vent stream coming from the 2nd separator flows, to measure the flow and quantify the amount of oxygen. The liquid effluent

(product) stream coming from the 2nd separator was analyzed by Gas Chromatography (GC) with respect to the compounds contained therein and their respective amounts, concentrations.

Example 1: **Start-up process with feed propylene starting before start of feed of aqueous hydrogen peroxide solution**

Start-up stage

The reactor of Reference Example 1 was purged with nitrogen and pressurized at 20 bar. At the beginning ($t_{\text{start-up}} = 0$ h) methanol was fed with a flow rate of 370 g/h via the static mixer to the reaction tube, so that the reaction tube was initially flooded with methanol, wherein the feed direction was from the bottom to the top direction of the reaction tube. 15 minutes later ($t_{\text{start-up}} = 15$ minutes), propylene addition was started via the static mixer with a flow rate of 54 g/h, so that a combined stream comprising methanol and propylene was fed to the reaction tube. After further 15 minutes ($t_{\text{start-up}} = 30$ minutes), feeding an aqueous hydrogen peroxide solution (40 weight-% H_2O_2) with a flow rate of 47 g/h (50% of the flow rate used for normal run) and additive solution (aqueous K_2HPO_4 solution, 0.3 weight-% K_2HPO_4) with a flow adjusted to maintain 130 micromol K^+ /mol hydrogen peroxide to the static mixer was begun, so that a combined stream of methanol, propylene, water, hydrogen peroxide and additive (K_2HPO_4) was fed to the reaction tube. – from that point in time, the time on stream was counted ($t_{\text{start-up}} = 30$ minutes corresponds to $t_{\text{on stream}} = 0$ h). After four hours on stream, the flow rate of the aqueous hydrogen peroxide solution was increased to 65 g/h (70% of the flow rate used for normal run) and the additive flow rate was increased accordingly to maintain 130 micromol K^+ /mol hydrogen peroxide in the combined feed stream. At 23 hours on stream, the flow rate of the aqueous hydrogen peroxide solution was increased to 94 g/h (100% of the flow rate used for normal run) and the additive flow rate was increased accordingly to maintain 130 micromol K^+ /mol hydrogen peroxide in the combined feed stream.

Normal run stage

The reaction was then carried on under normal run conditions with a combined feed stream to the reactor based on propylene fed with 54 g/h, aqueous H_2O_2 solution (40 weight-% H_2O_2) fed with a flow rate of 94 g/h, methanol fed with a flow rate of 370 g/h and additive solution 4 g/h aqueous K_2HPO_4 solution (0.3 weight-% K_2HPO_4), wherein the flow of the additive solution was adjusted to maintain 130 micromol K^+ /mol hydrogen peroxide. The normal run was continued at least until 72 h on stream.

During start-up stage and normal run stage -for the first 48 hours on stream- the water temperature setpoint was kept constant at 30 °C and only afterwards it was increased to reach a hydrogen peroxide conversion of 90% by using a cooling jacket circuit with water.

- 5 During start-up stage and normal run stage, samples were taken from the liquid effluent (product) stream downstream of the 2nd separator at a time on stream of 7 h, 23 h, 31 h, 47 h, 55 h and 71 h and analyzed via GC.

10 The selectivities to propylene oxide (PO) and several characteristic by-products were calculated based on the amount of PO or the respective by-product in the effluent stream taken from the reactor per hour relative to the total amount of propylene (C₃) converted into PO and all by-products per hour according to Equation (II). The results are shown below in Table 1 and are graphically represented in Fig. 1 (PO selectivity) and Fig. 3 (overview of average selectivities listed in Table 1 for AA, PM-2, PM-1, acetol, MPG and ROOH).

15 Hydrogen peroxide conversion was calculated based on the amount of hydrogen peroxide comprised in the effluent stream taken from the reactor relative to the amount of hydrogen peroxide comprised in the liquid feed stream provided to the reactor according to Equation (I) and the results are graphically shown in Fig. 2.

20

Table 1

Selectivities to PO and to by-products

Time [h]	PO [%]	AA [%]	PM-2 [%]	PM-1 [%]	Acetol [%]	MPG [%]	ROOH [%]
7	92.78	0.26	2.53	3.61	0.10	0.72	0.00
23	94.25	0.31	1.84	2.57	0.12	0.51	0.40
31	95.09	0.38	1.55	1.84	0.13	0.44	0.57
47	96.17	0.35	1.01	0.96	0.16	0.29	1.06
55	96.26	0.41	1.03	0.97	0.18	0.29	0.86
71	96.56	0.42	0.96	0.90	0.18	0.27	0.71
Average	95.19	0.36	1.49	1.81	0.15	0.42	0.60

Time on-stream time in hours

PO [%] Propylene based selectivity to PO in mol-%

AA [%] Propylene based selectivity to acetaldehyde in mol-%

PM-2 [%] Propylene based selectivity to 1-methoxy-2-methanol in mol-%

PM-1 [%] Propylene based selectivity to 2-methoxy-1-methanol in mol-%

Acetol [%] Propylene based selectivity to hydroxyacetone in mol-%

MPG [%] Propylene based selectivity to 1,2-propanediol in mol-%

ROOH [%] Propylene based selectivity to hydroperoxypropanols in mol-%

Comparative Example 1: Start-up process with feed of aqueous hydrogen peroxide solution starting before start of feed propylene

Start-up stage

5

The reactor of Reference Example 1 was purged with nitrogen and pressurized at 20 bar. At the beginning ($t_{\text{start-up}} = 0$ h) methanol was fed with a flow rate of 370 g/h via the static mixer to the reaction tube, so that the reaction tube is initially flooded with methanol, wherein the feed direction was from the bottom to the top direction of the reaction tube. After 15 minutes ($t_{\text{start-up}} = 15$ minutes), feeding an aqueous hydrogen peroxide solution (40 weight-% H_2O_2) with a flow rate of 47 g/h (50% of the flow rate used for normal run) and additive solution (aqueous K_2HPO_4 solution, 0.3 weight-% K_2HPO_4) with a flow adjusted to maintain 130 micromol K^+ /mol hydrogen peroxide to the static mixer was begun, so that a combined stream of methanol, water, hydrogen peroxide and additive (K_2HPO_4) was fed to the reaction tube. After further 15 minutes ($t_{\text{start-up}} = 30$ minutes), propylene was added via the static mixer with a flow rate of 54 g/h, so that a combined stream comprising methanol, hydrogen peroxide, water, K_2HPO_4 and propylene was fed to the reaction tube – from that point in time, the time on stream was counted ($t_{\text{start-up}} = 30$ minutes corresponds to $t_{\text{on stream}} = 0$ h). After four hours on stream ($t_{\text{on-stream}} = 4$ h), the flow rate of the aqueous hydrogen peroxide solution was increased to 65 g/h (70% of the flow rate used for normal run) and the additive flow rate was increased accordingly to maintain 130 micromol K^+ /mol hydrogen peroxide in the combined feed stream. At 24 hours on stream ($t_{\text{on-stream}} = 24$ h), the flow rate of the aqueous hydrogen peroxide solution was increased to 94 g/h (100% of the flow rate used for normal run) and the additive flow rate was increased accordingly to maintain 130 micromol K^+ /mol hydrogen peroxide in the combined feed stream.

25

Normal run stage

The reaction was then carried on under normal run conditions with a combined feed stream to the reactor based on propylene fed with 54 g/h, aqueous H_2O_2 solution (40 weight-% H_2O_2) fed with a flow rate of 94 g/h, methanol fed with a flow rate of 370 g/h and additive solution 4 g/h aqueous K_2HPO_4 solution (0.3 weight-% K_2HPO_4), wherein the flow of the additive solution was adjusted to maintain 130 micromol K^+ /mol hydrogen peroxide. The normal run was continued at least until 72 h on stream.

35

During start-up stage and normal run stage -for the first 48 hours on stream- the water temperature setpoint was kept constant at 30 °C and only afterwards it was increased to reach the target hydrogen peroxide conversion of 90% by using a cooling jacket circuit with water.

During start-up stage and normal run stage, samples were taken from the effluent (product) stream downstream of the 2nd separator at a time on stream of 8 h, 24 h, 32 h, 48 h, 56 h and 72 h.

- 5 The selectivities to propylene oxide (PO) and several characteristic by-products were calculated based on the amount of PO or the respective by-product in the effluent stream taken from the reactor relative to the total amount of PO and all by-products according to Equation (II). The results are shown below in Table 2 and are graphically represented in Fig. 1 (PO selectivity) and Fig. 3 (overview of average selectivities listed in Table 1 for AA, PM-2, PM-1, acetol, MPG and ROOH).
- 10

- Hydrogen peroxide conversion was calculated based on the amount of hydrogen peroxide comprised in the effluent stream taken from the reactor relative to the amount of hydrogen peroxide comprised in the liquid feed stream provided to the reactor according to Equation (I) and the results are graphically shown in Fig. 2.
- 15

Table 2

Selectivities to PO and to by-products

Time [h]	PO [%]	AA [%]	PM-2 [%]	PM-1 [%]	Acetol [%]	MPG [%]	ROOH [%]
8	91.99	0.29	2.76	4.12	0.11	0.73	0.00
24	93.77	0.39	1.76	2.41	0.16	0.58	0.93
32	94.60	0.40	1.51	1.56	0.22	0.50	1.21
48	95.69	0.47	1.32	1.25	0.24	0.35	0.68
56	96.00	0.51	1.13	1.09	0.23	0.34	0.70
72	96.00	0.61	1.11	1.02	0.26	0.34	0.66
Average	94.68	0.45	1.60	1.91	0.20	0.47	0.70

Time on-stream time in hours

PO [%] Propylene based selectivity to PO in mol-%

AA [%] Propylene based selectivity to acetaldehyde in mol-%

PM-2 [%] Propylene based selectivity to 1-methoxy-2-methanol in mol-%

PM-1 [%] Propylene based selectivity to 2-methoxy-1-methanol in mol-%

Acetol [%] Propylene based selectivity to hydroxyacetone in mol-%

MPG [%] Propylene based selectivity to 1,2-propanediol in mol-%

ROOH [%] Propylene based selectivity to hydroperoxypropanols in mol-%

Example 2: **Start-up process with feed propylene starting before start of feed of aqueous hydrogen peroxide solution – exceeding molar amount of propylene compared to hydrogen peroxide provided or intended to be provided respectively**

Start-up stage

The reactor of Reference Example 1 was purged with nitrogen and pressurized at 20 bar. At the beginning ($t_{\text{start-up}} = 0$ h) methanol was fed with a flow rate of 370 g/h via the static mixer to the reaction tube, so that the reaction tube was initially flooded with methanol, wherein the feed direction was from the bottom to the top direction of the reaction tube. 15 minutes later ($t_{\text{start-up}} = 15$ minutes), propylene addition was started via the static mixer with a flow rate of 17 g/h, so that a combined stream comprising methanol and propylene was fed to the reaction tube; the molar ratio propene : hydrogen peroxide (intended to be provided in normal run) was 0.3. After further 15 minutes ($t_{\text{start-up}} = 30$ minutes), feeding an aqueous hydrogen peroxide solution (40 weight-% H_2O_2) with a flow rate of 55 g/h and additive solution (aqueous K_2HPO_4 solution, 0.3 weight-% K_2HPO_4) with a flow adjusted to maintain 130 micromol K^+ /mol hydrogen peroxide to the static mixer was begun; simultaneously, the propylene feed was increased to 44 g/h, so that a combined stream of methanol, propylene, water, hydrogen peroxide and additive (K_2HPO_4) was fed to the reaction tube – from that point in time, the time on stream was counted ($t_{\text{start-up}} = 30$ minutes corresponds to $t_{\text{on stream}} = 0$ h); the molar ratio propene : hydrogen peroxide was 1.6. After four hours on stream, the flow rate of the aqueous hydrogen peroxide solution was increased to 80 g/h and the additive flow rate was increased accordingly to maintain 130 micromol K^+ /mol hydrogen peroxide in the combined feed stream, while simultaneously, the propylene feed was increased to 56 g/h; the molar ratio propylene : hydrogen peroxide was 1.4. At 23 hours and 45 minutes on stream, the flow rate of the aqueous hydrogen peroxide solution was increased to 94 g/h (100% of the flow rate used for normal run) and the additive flow rate was increased accordingly to maintain 130 micromol K^+ /mol hydrogen peroxide in the combined feed stream, while simultaneously, the propylene feed was increased to 66 g/h (100% of the flow rate used for normal run); the molar ratio propylene : hydrogen peroxide was 1.3.

Normal run stage

The reaction was then carried on under normal run conditions with a combined feed stream to the reactor based on propylene fed with 54 g/h, aqueous H_2O_2 solution (40 weight-% H_2O_2) fed with a flow rate of 94 g/h, methanol fed with a flow rate of 370 g/h and additive solution 4 g/h aqueous K_2HPO_4 solution (0.3 weight-% K_2HPO_4), wherein the flow of the additive solution was

adjusted to maintain 130 micromol K⁺/mol hydrogen peroxide. The normal run was continued at least until 72 h on stream.

During start-up stage and normal run stage -for the first 48 hours on stream- the water temperature setpoint was kept constant at 30 °C and only afterwards it was increased to reach a hydrogen peroxide conversion of 90% by using a cooling jacket circuit with water.

During start-up stage and normal run stage, samples were taken from the liquid effluent (product) stream downstream of the 2nd separator at a time on stream as indicated in Table 3 and analyzed via GC.

The selectivities to propylene oxide (PO) and several characteristic by-products were calculated based on the amount of PO or the respective by-product in the effluent stream taken from the reactor per hour relative to the total amount of propylene (C₃) converted into PO and all by-products per hour according to Equation (II). For PO, the average propylene based selectivity was 95.3 % (mol-%), whereas for the by-products AA, PM-1, PM-2 and acetol, the average selectivities were AA: 0.18 % (mol-%), OM-2: 1.66 % (mol-%), PM-1 2.02 % (mol-%) and acetol: 0.09 % (mol-%).

Hydrogen peroxide conversion was calculated based on the amount of hydrogen peroxide comprised in the effluent stream taken from the reactor relative to the amount of hydrogen peroxide comprised in the liquid feed stream provided to the reactor according to Equation (I).

Results – Comparison of procedures according to Examples 1 and 2 versus procedure according to Comparative Example 1

In the start-up procedure according to Example 1, based on an initial methanol stream, the feeding of propylene was started prior to start of the feeding of the aqueous hydrogen peroxide solution, whereas in Comparative Example 1, the start-up procedure was done the other way round, i.e. based on an initial methanol stream, the feeding of the aqueous hydrogen peroxide solution was started prior to start of the feeding of propylene.

The propylene oxide (PO) selectivity based on the propylene converted was always higher when following the procedure of Example 1 compared to Comparative Example 1, which indicated that a start-up with start of propylene feed prior to start of hydrogen peroxide feed was superior.

Regarding hydrogen peroxide conversion, it was seen that the hydrogen peroxide conversion was 100% in the first 24 hours on stream and almost identical (~97-98%) after 32 hours on stream for Example 1 and Comparative Example 1. Even if for the first 48 hours on stream the water temperature setpoint was kept constant at 30 °C and only afterwards it was increased to reach the target hydrogen peroxide conversion of 90%, a higher drop in hydrogen peroxide conversion was observed after these first 48 hours on stream - and prior to start of increase of the water temperature- in the procedure according to Comparative Example 1 (88%) in comparison to the procedure of Example 1 (93%). This shows that a start-up with start of hydrogen peroxide feed prior to start of propylene feed resulted in a faster catalyst deactivation.

Regarding the selectivities over the time for the main by-products acetaldehyde (AA), 1-methoxy-2-propanol (PM-2), 2-methoxy-1-propanol (PM-1), hydroxyacetone (acetol), 1,2-propane diol (MPG) and hydroperoxypropanols (ROOH), it was seen that the average selectivity to each by-product was always higher when the procedure of Comparative Example 1 was used in comparison to the procedure according to Example 1. This demonstrated that a start-up with start of hydrogen peroxide feed prior to start of propylene feed resulted in an increased by-products formation.

Looking further to Example 2, it was apparent that when comparing Example 1 and Example 2, Example 2, which was based on a start of propylene prior to start of hydrogen peroxide, combined with a step-wise increase of propylene and hydrogen peroxide under consideration of a molar excess of propylene vis-à-vis hydrogen peroxide used or intended to be used in the range of from 0.1:1 to 4:1 – here 0.3 - and preferably also a molar ratio of olefin : hydrogen peroxide once the hydrogen peroxide feed was started in the range of from 1.1:1 to 5:1 – here 1.6:1, 1.4:1 and 1.3:1 respectively -, resulted in a still further improved performance: While the PO selectivity was as good as in Example 1, the selectivities with respect to four of the main by-products, namely acetaldehyde (AA), 1-methoxy-2-propanol (PM-2), 2-methoxy-1-propanol (PM-1), hydroxyacetone (acetol), were drastically reduced.

Overall, it was shown that using a start-up procedure with start of propylene feed prior to start of hydrogen peroxide feed helped significantly to minimize the propylene oxide losses during the start-up phase and was thus superior to a start-up procedure with start of hydrogen peroxide feed prior to start of propylene feed.

Short description of the Figures

Fig. 1 shows the PO selectivity achieved according to the procedure of Example 1 over time versus the PO selectivity achieved according to the procedure of Comparative Example

1 over time, wherein the time on stream is shown on the x axis in hours and the PO selectivity in % is shown on the y axis.

- 5 Fig. 2 shows the hydrogen peroxide conversion achieved according to the procedure of Example 1 over time versus the hydrogen peroxide conversion achieved according to the procedure of Comparative Example 1 over time, wherein the time on stream is shown on the x axis in hours and the hydrogen peroxide conversion in % is shown on the y axis.
- 10 Fig. 3 shows the average selectivities for several by-products achieved according to the procedure of Example 1 versus the average selectivities for these by-products achieved according to the procedure of Comparative Example 1.

Cited Literature

15

- WO 2017/162446 A1
- WO 2022/263437 A1

Claims

1. A start-up method for a process for preparing an olefin oxide comprising a normal run stage, wherein the normal run stage comprises providing olefin, hydrogen peroxide and organic solvent into an epoxidation zone comprising an heterogeneous epoxidation catalyst, so that a reaction mixture comprising olefin, hydrogen peroxide and organic solvent is formed and subjecting the reaction mixture to epoxidation reaction conditions in the epoxidation zone, thereby obtaining a mixture comprising olefin oxide and organic solvent; wherein the start-up method comprises
- 5
- 10 (a) providing olefin and organic solvent for a first period of time P_1 to the epoxidation zone, so that a first mixture 1 is formed, which is essentially free of hydrogen peroxide, and contacting the first mixture 1 over P_1 under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst;
- 15 (b) after the first period of time providing olefin, organic solvent and hydrogen peroxide to the epoxidation zone for a second period of time P_2 , so that a second mixture 2 is formed, which comprises olefin, organic solvent, and hydrogen peroxide, and contacting the second mixture 2 over P_2 under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst;
- 20 wherein the amount of olefin provided in (a) is lower than the amount intended to be provided in the normal run stage.
2. The start-up method of claim 1, wherein the amounts of olefin and of hydrogen peroxide provided in (b) are lower than the respective amounts intended to be provided in the normal run stage, wherein preferably, the molar amount of olefin provided in (b) is higher than the molar amount of hydrogen peroxide provided in (b).
- 25
3. The start-up method of any claim 1 or 2, wherein (b) comprises
- 30 (b') after the first period of time P_1 , providing organic solvent and olefin and hydrogen peroxide in initial amounts to the epoxidation zone for a period of time P_2' , so that a mixture is formed, which comprises organic solvent, olefin, and hydrogen peroxide, wherein the amounts of the hydrogen peroxide and of the olefin are lower than the amounts intended to be provided in the normal run stage, and increasing the amount of the hydrogen peroxide and the amount of the olefin over the period of time P_2' up to the amounts intended to be provided in the normal run stage, so that a mixture 2' is formed, and contacting the mixture 2' over P_2' under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst; wherein preferably, the molar amount of olefin initially provided
- 35

is higher than the molar amount of hydrogen peroxide initially provided and the molar amount of olefin provided during the increase is higher than the molar amount of hydrogen peroxide provided during the increase.

- 5 4. The start-up method of any one of claims 1 to 3, wherein the olefin is provided in (a) in a molar ratio relative to the molar amount of hydrogen peroxide intended to be used in the normal run stage in the range of from 0.1:1 to 4:1, preferably in the range of from 0.1:1 to 1:1 or in the range of from 2:1 to 4:1.
- 10 5. The start-up method of any one of claims 1 to 4, wherein the olefin and the hydrogen peroxide are provided in (b) or in (b') respectively so that the molar ratio of olefin : hydrogen peroxide in the second mixture 2 formed in (b) or in the mixture formed in (b') respectively is in the range of from 1.1:1 to 5:1, preferably in the range of from 1.1:1 to 2:1 or in the range of from 3:1 to 5:1.
- 15
6. The start-up method of any one of claims 1 to 5, wherein (b) comprises
- 20 (b.1) after the first period of time providing olefin, organic solvent and hydrogen peroxide to the epoxidation zone for a second period of time P_2 , so that a second mixture 2 is formed, which comprises olefin, organic solvent, and hydrogen peroxide, and contacting the second mixture 2 over P_2 under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst;
- 25 (b.2) removing during the respective period of time an effluent stream from the epoxidation zone, the effluent stream comprising olefin oxide and organic solvent; and/or wherein (b') comprises
- 30 (b'.1) after the first period of time P_1 , providing organic solvent and olefin and hydrogen peroxide in initial amounts to the epoxidation zone for a period of time P_2' , so that a mixture is formed, which comprises organic solvent, olefin, and hydrogen peroxide, wherein the amounts of the hydrogen peroxide and of the olefin are lower than the amounts intended to be provided in the normal run stage, and increasing the amount of the hydrogen peroxide and the amount of the olefin over the period of time P_2' up to the amounts intended to be provided in the normal run stage, so that a mixture 2' is formed, and contacting the mixture 2' over P_2' under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst;
- 35 (b'.2) removing during the respective period of time an effluent stream from the epoxidation zone, the effluent stream comprising olefin oxide and organic solvent.

7. The start-up method of any one of claims 1 to 6, wherein in any one of (a), (a.1), (b), (b'), (b.1), (b'.1), preferably in at least one of (b), (b'), (b.1), (b'.1), more preferably in each of (b), (b'), (b.1), (b'.1), an additive is provided to the epoxidation zone, wherein the additive is selected from the group consisting of potassium salt of an inorganic acid, potassium salt of an organic acid, ammonia, ammonium salt of an inorganic acid, ammonium salt of an organic acid and mixtures of two or more thereof;
- 5
- wherein the additive is preferably selected from the group consisting of potassium dihydrogen phosphate, dipotassium hydrogen phosphate, potassium formate, potassium acetate, potassium hydrogen carbonate, dipotassium etidronate, ammonium dihydrogen phosphate, diammonium hydrogen phosphate, ammonia and mixtures of two or more thereof,
- 10
- more preferably from the group consisting of potassium dihydrogen phosphate, dipotassium hydrogen phosphate, dipotassium etidronate, ammonia and mixtures of two or more thereof;
- 15
- wherein the additive more preferably comprises at least dipotassium etidronate or dipotassium hydrogen phosphate or a mixture of dipotassium etidronate and dipotassium hydrogen phosphate, wherein more preferably in the range of from 95 to 100 weight-% of the additive are dipotassium etidronate or dipotassium hydrogen phosphate or a mixture of dipotassium etidronate and dipotassium hydrogen phosphate.
- 20
8. The start-up method of claim 7, wherein the additive is in case of ammonia provided in pure form or in aqueous solution, wherein the additive is in case of being selected from the group consisting of potassium salt of an inorganic acid, potassium salt of an organic acid, ammonium salt of an inorganic acid, ammonium salt of an organic acid or any mixture comprising two or more thereof or any mixture comprising ammonia and at least one thereof provided in aqueous solution;
- 25
- wherein the additive in aqueous solution releases or forms one or more cation(s) M, wherein M represents in case of a potassium salt K^+ , or, in case of ammonia or ammonium salts, M represents the sum of NH_4^+ and NH_3 .
- 30
9. The start-up method of any one of claims 1 to 8 further comprising before (a)
- (x) providing an organic solvent stream for a period of time P_x to the epoxidation zone,
- 35
- wherein P_x is preferably a period of time in the range of from 10 minutes to 24 hours.
10. A process for preparing an olefin oxide comprising a normal run stage and a start-up stage, wherein the normal run stage comprises

- (A) providing olefin, hydrogen peroxide, water and organic solvent into an epoxidation zone comprising an heterogeneous epoxidation catalyst, so that a reaction mixture comprising olefin, hydrogen peroxide, water and organic solvent is formed;
- 5 (B) subjecting the reaction mixture from (A) to epoxidation reaction conditions in the epoxidation zone, thereby obtaining a mixture comprising olefin oxide, water and organic solvent;
- (C) removing an effluent stream from the epoxidation zone, comprising olefin oxide, water and organic solvent;
- wherein the start-up stage comprises
- 10 (a) providing olefin and organic solvent for a first period of time P_1 to the epoxidation zone, so that a first mixture 1 is formed, which is essentially free of hydrogen peroxide, and contacting the first mixture 1 over P_1 under epoxidation reaction conditions in the epoxidation zone with the heterogeneous epoxidation catalyst,
- 15 wherein the amount of olefin provided in (a) is lower than the amount provided in the normal run stage;
- (b) after the first period of time providing organic solvent, olefin and hydrogen peroxide to the epoxidation zone for a second period of time P_2 , so that a second mixture 2 is formed, which comprises olefin, organic solvent, and hydrogen peroxide, and contacting the second mixture 2 over P_2 under epoxidation reaction conditions in the
- 20 epoxidation zone with the heterogeneous epoxidation catalyst.
11. Olefin oxide, preferably propylene oxide, obtained or obtainable from the process of claim 10.