Method for the regeneration of a catalyst

The invention relates to a method for the regeneration of a catalyst, in particular a zeolite containing titanium atoms which is used as a catalyst for the preparation of epoxides from olefins and hydrogen peroxide.

The preparation of epoxides from olefins by converting the olefin to the epoxide by means of hydrogen peroxide in the presence of a zeolite containing titanium atoms as catalyst is known (EP-A 0 100 119). M. G. Clerici, G. Bellussi and U. Romano , J. Catal. 129 (1991) 159-167 show moreover that the titanium-containing zeolite rapidly loses catalytic activity during its use as a catalyst for the epoxidation of propylene oxide. Clerici et al. describe two possible methods of regenerating the activity of the catalyst.

On the one hand the zeolite can be regenerated by calcining at 550°C, on the other hand the catalytic activity can be restored by washing with solvents at elevated temperature, preferably with methanol or with the solvent used for the epoxidation. Regeneration by calcining has the disadvantage that for this purpose the catalyst has first of all to be dried, then heated to the high calcining temperature and subsequently cooled again, which results in a considerable additional energy requirement and expenditure of apparatus. Regeneration by washing with a solvent is a slow process, which as a rule requires considerably more time than the actual epoxidation reaction.

The object was therefore to find a method for the regeneration of a catalyst which can be carried out quickly and easily.

The invention provides a method for the regeneration of a catalyst, in particular a zeolite containing titanium atoms used as a catalyst for the preparation of epoxides from olefins and hydrogen peroxide, which is characterised in that the catalytic activity of the spent catalyst is regenerated by treatment with hydrogen peroxide in the absence of olefins and the regenerated catalyst is used again for the epoxidation of olefins.

The epoxidation of an olefin, preferably of propylene, is carried out, as described in EP 100 119, with preferably methanol being used as solvent. The zeolite catalyst containing titanium atoms is used for the epoxidation, the catalytic activity whereof is completely or partly exhausted during the reaction, is subsequently separated from the reaction mixture and optionally washed with a solvent, preferably with water. The spent catalyst is afterwards reacted with a solution of hydrogen peroxide in a solvent, preferably water. Here the quantity of hydrogen peroxide is so chosen that it is more than ten times, preferably more than one hundred times, the quantity of olefin remaining in the catalyst and more than twice, preferably more than ten times, the quantity of titanium contained in the catalyst. The chosen concentration of the H_2O_2 solution used for the regeneration can be between 0.01 and 70 wt.%, preferably between 1 and 45 wt.%. The regeneration can be carried out at temperatures of between 0 and 200°C, preferably between 40 and 120°C. In a preferred embodiment of the invention the regeneration can be carried out at the boiling point of the aqueous H_2O_2 solution. The time necessary for the regeneration varies with the regeneration temperature applied and the concentration of H_2O_2 and can be so chosen that the required degree of regeneration is achieved.

Afterwards the catalyst is separated from the regenerating solution and optionally washed with a solvent, preferably water. It can be returned to the epoxidation reaction.

If the solvent used in the regeneration is also used in the epoxidation reaction then the catalyst, without prior separation, can be returned to the epoxidation reaction together with the hydrogen peroxide solution used for the regeneration.

If only a partial regeneration of the catalyst is required, the regeneration according to the invention can also be carried out in a way such that the quantity of catalyst separated from the reaction mixture is divided into two portions, only one of the portions is regenerated using hydrogen peroxide and the two portions are returned together or separately to the epoxidation reaction.

According to the invention the catalyst used can be titanium silicalite in the form of a suspension consisting alternatively of pure titanium silicalite, titanium silicalite containing a binder or titanium silicalite on an organic or inorganic supporting material. The epoxidation of the olefin, preferably of propylene, is carried out according to EP 100 119, with preferably methanol being used as solvent. Stirred-tank reactors, tubular loop reactors, bubble columns, continuous-flow reactors or other suitable reactors for suspensions, as well as combinations of these reactors, can be employed to carry out the epoxidation, with the selection of the reactor type being made by the person skilled in the art appropriately to the reaction conditions selected and the olefin being epoxidised. The catalyst is subsequently separated from the reaction mixture by filtration, centrifugation, decantation or other suitable method and

washed with a solvent, preferably water. The catalyst can then again be suspended in an aqueous hydrogen peroxide solution having a concentration of between 0.01 and 70 wt.%, preferably between 1 and 45 wt.%, particularly preferably between 10 and 45 wt.%, and the suspension maintained at a temperature of between 0 and 150°C, preferably between 40 and 120°C. The contact time for the regeneration of the catalyst is so chosen that the required degree of regeneration, preferably between 20 and 100% of the initial catalytic activity, is achieved. The newly regenerated catalyst is subsequently returned to the epoxidation reaction, with the hydrogen peroxide solution used for the regeneration optionally being completely or partly separated. In the preferred use of aqueous hydrogen peroxide solutions having a hydrogen peroxide content of between 10 and 45 wt.% for the regeneration, the suspension of the catalyst in the regenerating solution can advantageously be passed to the epoxidation reaction without separation of the catalyst, so that the hydrogen peroxide not used for regeneration is utilised for epoxidising the olefin.

In another preferred embodiment of the invention, for the epoxidation of the olefin a titanium silicalite shaped with a binder is used as a catalyst in the form of a fixed bed. In this case the catalyst packing is used for the epoxidation until the activity of the catalyst is completely or partly exhausted. Thereafter the catalyst packing is optionally washed with a solvent, preferably water. An aqueous hydrogen peroxide solution having a hydrogen peroxide content of between 0.01 and 70 wt.%, preferably between 1 and 40 wt.%, is then passed at a temperature of between 0 and 150°C, preferably between 40 and 120°C, over the catalyst packing until the required degree of regeneration is achieved. Here the hydrogen

peroxide solution used for the regeneration can advantageously be circulated over the catalyst packing. Thereafter the catalyst packing is used again for epoxidising the olefin, optionally after intermediate washing with a solvent.

The method according to the invention for the preparation of epoxides from olefins and hydrogen peroxide using zeolite catalysts containing titanium atoms and a regeneration of the catalyst by treatment of the catalyst with hydrogen peroxide in the absence of the olefin, compared with the known prior art methods for the regeneration of the catalyst by calcining or by washing with solvents, has the advantage of an easier, quicker and distinctly better regeneration and return of the catalyst to the epoxidation reaction. It permits a more economical preparation of epoxides from olefins and hydrogen peroxide than do the known methods.

Examples

Example 1

Determination of the catalytic activity of titanium silicalite in the epoxidation of propylene

1 g of titanium silicalite in 300 ml of methanol is placed in a thermostatted laboratory autoclave equipped with a gas dispersing stirrer at 40°C under a propylene atmosphere and is saturated with propylene at an excess pressure of 3 bar. 12.9 g of 30 wt.% aqueous hydrogen peroxide solution is then added in one portion, with stirring, and the reaction mixture maintained at 40°C and 3 bar, with further propylene being added via a pressure regulator in order to compensate for consumption owing to the reaction. At regular intervals

samples are withdrawn through a filter and the hydrogen peroxide content of the reaction mixture is determined by redox titration with cerium(IV) sulphate solution. Plotting of ln (c/c_o) against the time t, with c being the measured H_2O_2 concentration at the time t and c_o being the calculated H_2O_2 concentration at the start of the reaction, produces a straight line. The activity index k is determined from the gradient of this line by means of the relation

$\frac{dc}{dt} = -k.c.c_{cat}$, wherein c_{cat} represents the concentration of of catalyst in kg of catalyst per kg of reaction mixture. The activity index increases with increasing catalytic activity of the catalyst in the epoxidation of propylene.

Example 2

Catalytic activity of fresh titanium silicalite

The activity of titanium silicalite, prepared according to the instructions in J.P.A. Martens et al., Appl. Catal. A99 (1993), 71 - 84, is examined as described in Example 1. An activity index of 18.9 min^{-1} is determined.

Example 3

Loss of activity of titanium silicalite through use as catalyst for the epoxidation of propylene

5 g of titanium silicalite, obtained as mentioned in Example 2, in 270 g of methanol is placed in a thermostatted laboratory autoclave equipped with a gas dispersing stirrer at 40°C under a propylene atmosphere and is saturated with propylene at

an excess pressure of 3 bar. A mixture of 560 g of 50 wt.% hydrogen peroxide and 3600 g of methanol is then added at a rate of 600 g/h, with stirring, and simultaneously the reaction mixture is withdrawn through a filter in a quantity such that the weight of the contents of the reactor remains constant. In the course of this the catalyst is retained in the reactor by the filter. During the metered addition of hydrogen peroxide, further propylene is added via a pressure regulator in order to maintain the pressure in the reactor constant. After 7 hours the metered addition of hydrogen peroxide is terminated, the catalyst is filtered off, washed with methanol at 20°C and dried by exposure to air at 20°C. The activity of the spent catalyst is examined as in Example 1. An activity index of 1.3 min^{-1} is determined. A repetition of the activity test according to Example 1 after 5 days produces an activity index of 1.7 min^{-1}. The activity indices established of 1.3 min^{-1} and 1.7 min^{-1} respectively show that titanium silicalite, when employed as catalyst for the epoxidation of propylene using hydrogen peroxide, largely loses its catalytic activity in this reaction and does not recover its catalytic activity without measures for regeneration being taken.

Examples 4 and 5 (Comparative Examples)

Regeneration of spent titanium silicalite by boiling with methanol or water

Example 4

1 g of spent titanium silicalite catalyst from Example 3 is heated under reflux for 4 h in 25 ml of methanol and then filtered. The catalytic activity is examined as in Example 1. An activity index of 1.3 min^{-1} is determined.

Example 5

1 g of spent titanium silicalite catalyst from Example 3 is heated under reflux for 4 h in 25 ml of demineralised water, subsequently filtered and then washed with methanol. The catalytic activity is examined as in Example 1. An activity index of 1.6 min^{-1} is determined.

Examples 4 and 5 show that a regeneration of spent titanium silicalite by boiling respectively with methanol at 65°C and with water at 100°C for a period of 4 h brings about no appreciable improvement in the catalytic activity.

Examples 6 - 8 (according to the invention)

Regeneration of spent titanium silicalite by boiling with hydrogen peroxide

Example 6

1 g of spent titanium silicalite catalyst from Example 1 is heated under reflux for 4 h in 25 ml of 5 wt.% of aqueous hydrogen peroxide solution, subsequently filtered and then washed with water and methanol. The catalytic activity is examined as in Example 1. An activity index of 18.3 min^{-1} is determined.

Example 7

Example 6 is repeated, with the treatment using hydrogen peroxide being shortened to 1 h. An activity index of 11.2 min^{-1} is determined.

Example 8

Example 6 is repeated, with the treatment using hydrogen peroxide being shortened to 15 min. An activity index of 4.9 min^{-1} is determined.

Examples 6 - 8 show that spent titanium silicalite can be completely regenerated by a treatment according to the invention using 5 wt.% of hydrogen peroxide at 100°C for a period of 4 h and that, by selecting the duration of treatment using hydrogen peroxide, a specific partial regeneration of the catalyst can be achieved.

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Claims

1. Method for the regeneration of a catalyst, in particular a zeolite containing titanium atoms used as a catalyst for the preparation of epoxides from olefins and hydrogen peroxide, characterised in that the catalytic activity of the spent catalyst is regenerated by treatment with hydrogen peroxide in the absence of olefins and the regenerated catalyst is used again for the epoxidation of olefins.

2. Method according to claim 1, characterised in that the spent catalyst is regenerated using an aqueous hydrogen peroxide solution which contains between 0.01 and 70 wt.% of hydrogen peroxide.

3. Method according to claim 2, characterised in that the spent catalyst is regenerated using an aqueous hydrogen peroxide solution which contains between 1 and 45 wt.% of hydrogen peroxide.

4. Method according to claims 1 to 3, characterised in that the regeneration is carried out at a temperature of between 0 and 200°C.

5. Method according to claim 4, characterised in that the regeneration is carried out at a temperature of between 40 and 120°C.

6. Method for the preparation of an epoxide by reacting an olefin with hydrogen peroxide in the presence of a zeolite containing titanium atoms as catalyst, characterised in that the catalytic activity of the spent catalyst is regenerated according to claims 1 to 5 by treatment with hydrogen peroxide in the absence

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of the olefin and the regenerated catalyst is used again for the epoxidation.

7. Method according to claim 6, characterised in that the olefin used is propylene.

8. Method according to claims 6 and 7, characterised in that the epoxidation reaction is carried out in a mixture of methanol and water as solvent.

9. Method according to claims 6 to 8, characterised in that the catalyst is used in the form of a suspension.

10. Method according to claims 6 to 9, characterised in that the spent catalyst is regenerated using an aqueous hydrogen peroxide solution which contains between 10 and 45 wt.% of hydrogen peroxide, and the mixture of catalyst and hydrogen peroxide from the regeneration is used in the epoxidation reaction without prior separation.

11. Method according to claim 6, characterised in that the catalyst is used in the form of a fixed bed.

12. Method according to claim 11, characterised in that during the regeneration the hydrogen peroxide solution is circulated over the fixed catalyst bed.

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