As suitable zeolitic materials, the zeolites known as TS-1 (titanium silicalite 1), TS-2 (titanium silicalite 2) and TS-3 (titanium silicalite 3) are disclosed. Further, a list of titanium containing molecular sieves having framework structure isomorphous to zeolite beta, mordenite, ZSM-48, ZSM-12, MCM-22 (MWW) and MCM-41 is described. According to these documents, it is especially preferred to employ the catalyst in epoxidation reactions where hydrogen peroxide is generated in situ. Therefore, the main focus of the documents is to be seen in catalysts which additionally contain a noble metal such as palladium. In this respect, reference is made to the working examples where exclusively a modified TS-1 catalyst is employed which was prepared by spray-drying a mixture comprising TS-1, colloidal silica binder and zinc oxide. Palladium as noble metal is then applied to the spray-dried product by ion exchange. This catalyst, i.e. the noble metal-treated spray-dried material, is then employed in an epoxidation reaction where methanol is used as solvent. With regard to the spray-drying step, it is disclosed in the working examples that the air feed temperature of the spray-drier is in the range of from 416 to 437 °C. As to the spray-dried material as such, the only information which is given is the chemical composition comprising 0.35 weight-% zinc.

It was an object of the embodiments disclosed herein to provide a novel micropowder comprising a zinc and titanium containing zeolitic material of structure type MWW which has advantageous characteristics, in particular when used as intermediate product for the preparation of a catalyst in the form of a molding.

It was another object of the embodiments disclosed herein to provide a novel molding comprising the novel micropowder, in particular a molding having advantageous properties, preferably if used in epoxidation reactions.

It was yet another object of the embodiments disclosed herein to provide a process for the preparation of said micropowder and said molding, in particular to provide a process resulting in a molding having advantageous properties, preferably if used in epoxidation reactions.

Surprisingly, it was found that a novel micropowder with particles exhibiting a specific size and pore characteristics represents such advantageous micropowder which is, in particular, a perfectly suitable intermediate for the preparation of a catalyst in the form of a molding.

As to said molding and the preparation thereof, it was found that by a specific post-treatment of a molding prepared based on said intermediate, the characteristics of the molding can be drastically improved, in particular in case the molding is employed as catalyst for the preparation of propylene oxide via epoxidation of propene.

Therefore, the present disclosure relates to a micropowder, the particles of which having a Dv10 value of at least 2 micrometer, said micropowder comprising mesopores having an average pore diameter (4V/A) in the range of from 2 to 50 nm as determined by Hg porosimetry according to DIN 66133, and comprising, based on the weight of the micropowder, at least 95 weight-% of a microporous aluminum-free zeolitic material of structure type MWW containing titanium and zinc (ZnTiMWW).

In an aspect, there is provided a micropowder, the particles of which having a Dv10 value of at least 2 micrometer, said micropowder comprising mesopores having an average pore diameter (4V/A) in the range of from 2 to 50 nm as determined by Hg porosimetry according to DIN 66133, and comprising, based on the weight of the micropowder, at least 95 weight-% of a microporous aluminum-free zeolitic material of structure type MWW containing titanium and zinc (ZnTiMWW), wherein the Dv10 value stands for the average particle size where 10 vol.-% of the particles of the micropowder have a smaller size.

In another aspect, there is provided a molding, comprising said micropowder, the molding preferably further comprising at least one binder, preferably a silica binder.

The present disclosure also relates to a process comprising

(i) providing a suspension containing a microporous aluminum-free zeolitic material of structure type MWW containing titanium and zinc (ZnTiMWW);
(ii) subjecting the suspension provided in (i) to spray-drying to obtain a micropowder;
(iii) optionally calcining the micropowder obtained in (ii).

In another aspect, there is provided a process comprising

(i) providing a suspension containing a microporous aluminum-free zeolitic material of structure type MWW containing titanium and zinc (ZnTiMWW);
(ii) subjecting the suspension provided in (i) to spray-drying to obtain a micropowder;
(iii) optionally calcining the micropowder obtained in (ii),

wherein the micropowder obtained in (ii) or (iii), preferably in (iii), is the micropowder as defined above.

The present disclosure also relates to said process, further comprising

(iv) shaping the micropowder obtained in (ii) or (iii) to obtain a molding;
(v) optionally drying and/or calcining the molding obtained in (iv).

The present disclosure also relates to said process, further comprising

(vi) subjecting the molding obtained in (iv) or (v), preferably in (v), to a water-treatment;
(vii) optionally drying and/or calcining the water-treated molding.

The present disclosure also relates to the use of said micropowder or of said molding as a catalyst, preferably as a catalyst for preparing propylene oxide from propene with hydrogen peroxide as oxidizing agent in acetonitrile as solvent.

In another aspect, there is also provided the use of the micropowder as defined above or of the molding as defined above, as a catalyst, preferably as a catalyst for preparing propylene oxide from propene with hydrogen peroxide as oxidizing agent in acetonitrile as solvent.

According to the present disclosure, it is conceivable that if hydrogen peroxide is used as oxidizing agent, the hydrogen peroxide is formed in situ during the reaction from hydrogen and oxygen or from other suitable precursors.

However, most preferably, the term "using hydrogen peroxide as oxidizing agent" as used in the context of the present disclosure relates to an embodiment where hydrogen peroxide is not formed in situ but employed as starting material, preferably in the form of a solution, preferably an at least partially aqueous solution, more preferably an aqueous solution, said preferably aqueous solution having a preferred hydrogen peroxide concentration in the range of from 20 to 60, more preferably from 25 to 55 weight-%, based on the total weight of the solution.

According to the present disclosure, a microporous aluminum-free zeolitic material of structure type MWW containing titanium and zinc (ZnTiMWW) is comprised in the inventive micropowder. The term "aluminum-free" as used in this context of the present disclosure relates to a ZnTiMWW which may contain aluminum only in traces as impurities which may result, for example, from aluminum impurities in the starting materials from which the ZnTiMWW is prepared. In particular, no aluminum source is used for the preparation of the ZnTiMWW. Typically, the aluminum-free ZnTiMWW according to the present disclosure contains at most 100 weight-ppm, preferably at most 50 weight-ppm of aluminum, based on the total weight of the ZnTiMWW.

The micropowder

As mentioned above, the present invention relates to a micropowder, the particles of which having a Dv10 value of at least 2 micrometer, said micropowder comprising mesopores having an average pore diameter (4V/A) in the range of from 2 to 50 nm as determined by Hg porosimetry according to DIN 66133, and comprising, based on the weight of the micropowder, at least 95 weight-% of a microporous aluminum-free zeolitic material of structure type MWW containing titanium and zinc (ZnTiMWW).

In the context of the present invention, it was surprisingly found that such a micropowder containing ZnTiMWW having particles with a certain particle size distribution is especially suitable for the preparation of a molding based on this micropowder. Due to a preferred use of the ZnTiMWW as catalytically active material, in particular in industrial-size processes, the preparation of such moldings was found to be of major importance since for example in continuous-type processes where the catalyst is employed as fixed-bed catalysts, moldings containing ZnTiMWW are one of the most preferred embodiments how the ZnTiMWW can be used as catalytically active material. Accordingly, it was found that the Dv10 values should have a certain minimum size which means that the micropowder should exhibit a certain minimum coarseness. Therefore, according to the present invention, the particles of the micropowder have a Dv10 value of at least 2 micrometer.

The term "Dv10 value" as referred to in the context of the present invention describes the average particle size where 10 vol.% of the particles of the micropowder have a smaller size. Similarly, the term "Dv50 value" as referred to in the context of the present invention describes the average particle size where 50 vol.% of the particles of the micropowder have a smaller size, and the term "Dv90 value" as referred to in the context of the present invention describes the average particle size where 90 vol.% of the particles of the micropowder have a smaller size. In particular, the Dv10, Dv50, and Dv90 values as referred to in the context of the present invention are to be understood as being

Claims

1. A micropowder, the particles of which having a Dv10 value of at least 2 micrometer, said micropowder comprising mesopores having an average pore diameter (4V/A) in the range of from 2 to 50 nm as determined by Hg porosimetry according to DIN 66133, and comprising, based on the weight of the micropowder, at least 95 weight-% of a microporous aluminum-free zeolitic material of structure type MWW containing titanium and zinc (ZnTiMWW), wherein the Dv10 value stands for the average particle size where 10 vol.-% of the particles of the micropowder have a smaller size.

2. The micropowder of claim 1, having a Dv10 value in the range of from 2 to 5.5 micrometer, preferably from 3 to 5.5 micrometer.

3. The micropowder of claim 1 or 2, having a Dv50 value in the range of from 7 to 25 micrometer, wherein the Dv50 value stands for the average particle size where 50 vol.-% of the particles of the micropowder have a smaller size.

4. The micropowder of any of claims 1 to 3, wherein the mesopores have an average pore diameter (4V/A) in the range of from 10 to 50 nm, preferably of from 15 to 40 nm, more preferably of from 20 to 30 nm, as determined by Hg porosimetry according to DIN 66133.

5. The micropowder of any of claims 1 to 4, additionally comprising macropores having an average pore diameter (4V/A) in the range of from more than 50 nm, said macropores preferably having an average pore diameter in the range of from 0.05 to 3 micrometer, as determined by Hg porosimetry according to DIN 66133.

6. The micropowder of any of claims 1 to 5, wherein the micropores of the ZnTiMWW have an average pore diameter in the range of from 1.0 to 1.2 nanometer as determined by nitrogen adsorption according to DIN 66135.

7. The micropowder of any of claims 1 to 6, comprising, based on the weight of the micropowder, at least 99 weight-%, preferably at least 99.7 weight-% of the ZnTiMWW.

8. The micropowder of any of claims 1 to 7, wherein the ZnTiMWW contains zinc in an amount of from 1.0 to 2.0 weight-%, preferably of from 1.2 to 1.9 weight-%, calculated as Zn and based on the weight of the ZnTiMWW.

9. The micropowder of any of claims 1 to 8, wherein the ZnTiMWW contains titanium in an amount of from 1.0 to 2.0 weight-%, preferably of from 1.2 to 1.8 weight-%, calculated as Ti and based on the weight of the ZnTiMWW.

10. The micropowder of any of claims 1 to 9, having a crystallinity, as determined by X-ray diffraction (XRD) analysis, of at least (80 +/- 10) %, preferably of at least (85 +/- 10) %.

11. The micropowder of any of claims 1 to 10, comprising, based on the total weight of the micropowder and calculated as element, less than 0.001 weight-%, preferably less than 0.0001 weight-% of a noble metal, preferably selected from the group consisting of gold, silver, platinum, palladium, iridium, ruthenium, osmium, and a mixture of two or more thereof, more preferably selected from the group consisting of gold, platinum, gold, and a mixture of two or more thereof.

12. The micropowder of any of claims 1 to 11, comprising, based on the total weight of the micropowder and calculated as element, less than 0.1 weight.-%, preferably less than 0.01 weight-% of boron.

13. The micropowder of any of claims 1 to 12, being a spray powder, obtainable or obtained by spray-drying.

14. A molding, comprising the micropowder according to any of claims 1 to 13, the molding preferably further comprising at least one binder, preferably a silica binder.

15. The molding of claim 14, comprising mesopores having an average pore diameter in the range of from 4 to 40 nm, preferably from 20 to 30 nm as determined by Hg porosimetry according to DIN 66133.

16. The molding of claim 14 or 15, having a crystallinity, as determined by XRD analysis, of at least (55 +/- 10) %, preferably in the range of from ((55 to 75) +/- 10) %.

17. The molding of any of claims 14 to 16, comprising the micropowder in an amount in the range of from 70 to 80 weight-% and the silica binder in an amount in the range of from 30 to 20 weight-%, the micropowder together with the silica binder constituting at least 99 weight-% of the molding, wherein the molding has a concentration of silanol groups with respect to the total number of Si atoms of at most 6 %, preferably at most 3 %, as determined according to ^{29}Si MAS NMR.

18. The molding of any of claims 14 to 17, being a strand having a circular cross-section and a diameter in the range of from 1.5 to 1.7 mm and having a crush strength of at least 5 N, preferably in the range of from 5 to 20 N, more preferably in the range of from 12 to 20 N, the crush strength being determined by crush strength test machine Z2.5/TS1S according to the method as described in the description.

19. The molding of any of claims 14 to 18, the ^{29}Si-NMR spectrum of said molding comprising six peaks at the following positions

peak 1 at -98 +/- x ppm,
peak 2 at -104 +/- x ppm,
peak 3 at -110 +/- x ppm,
peak 4 at -113 +/- x ppm,
peak 5 at -115 +/- x ppm,
peak 6 at -118 +/- x ppm,

with x in any of the peaks being 1.5, preferably 1.0, more preferably 0.5, wherein Q which is defined as

$$Q = 100 * \{ [a_1+a_2] / [a_4+a_5+a_6] \} / a_3$$

is at most 2.5, preferably at most 1.6, preferably at most 1.4, with $[a_1+a_2]$ being the sum of the peak areas of peaks 1 and 2, and $[a_4 + a_5 + a_6]$ being the sum of the peak areas of peaks 4, 5, and 6, and a_3 being the peak area of peak 3.

20. The molding of any of claims 14 to 19, having a water uptake in the range of from 3 to 8 weight-%, preferably from 4 to 7 weight-%.

21. The molding of any of claims 14 to 20, the infrared spectrum of said molding comprising a band in the region of (3700 - 3750) +/- 20 cm^{-1} and a band in the region of (3670 - 3690) +/- 20 cm^{-1}, wherein the intensity ratio of the band in the region of (3700 - 3750) +/- 20 cm^{-1} relative to the band in the region of (3670 - 3690) +/- 20 cm^{-1} is at most 1.5, preferably at most 1.4.

22. A process comprising
(i) providing a suspension containing a microporous aluminum-free zeolitic material of structure type MWW containing titanium and zinc (ZnTiMWW);
(ii) subjecting the suspension provided in (i) to spray-drying to obtain a micropowder;
(iii) optionally calcining the micropowder obtained in (ii),
wherein the micropowder obtained in (ii) or (iii), preferably in (iii), is the micropowder according to any of claims 1 to 13.

23. The process of claim 22, wherein the suspension provided in (i) has a solid content in the range of from 5 to 25 weight-%, preferably of from 10 to 20 weight-%, the suspension preferably being an aqueous suspension.

24. The process of claim 22 or 23, wherein the ZnTiMWW according to (i) contains zinc in an amount of from 1.0 to 2.0 weight-%, preferably of from 1.2 to 1.9 weight-%, calculated as Zn, and titanium in an amount of from 1.0 to 2.0 weight-%, preferably of from 1.2 to 1.8 weight-%, calculated as Ti and based on the weight of the ZnTiMWW.

25. The process of any of claims 22 to 24, wherein in (ii), a spray-apparatus, preferably a spray-tower is used for spray-drying the suspension, said apparatus having at least one spray-nozzle, preferably at least one two-component nozzle, said nozzle having a diameter in the range of from 3.5 to 4.5 mm.

26. The process of any of claims 22 to 25, wherein in (ii), a spray-apparatus, preferably a spray-tower is used for spray-drying the suspension, said apparatus being operated with a nozzle gas having a temperature in the range of from 20 to 50 °C, preferably of from 20 to 30 °C, and a drying gas having a temperature in the range

of from 250 to 350 °C, preferably of from 275 to 325 °C, said nozzle gas preferably being an inert gas, more preferably technical nitrogen, and said drying gas preferably being an inert gas, more preferably technical nitrogen.

27. The process of any of claims 22 to 26, wherein in (iii), the micropowder is calcined at a temperature in the range of from 600 to 700 °C for a duration in the range of from 0.5 to 6 h.

28. The process of any of claims 22 to 27, further comprising
(iv) shaping the micropowder obtained in (ii) or (iii) to obtain a molding;
(v) optionally drying and/or calcining the molding obtained in (iv).

29. The process of claim 28, wherein the shaping according to (iv) comprises
(aa) mixing the micropowder with a binder or a binder precursor, preferably a silica binder or a silica binder precursor, wherein the weight ratio of the ZnTiMWW contained in the micropowder relative to silica contained in or resulting from the silica binder is in the range of from 3:7 to 1:4, to obtain a mixture;
(bb) shaping the mixture obtained in (aa) to obtain the molding, said shaping preferably comprising subjecting the mixture obtained in (aa) to extrusion from which preferably strands are obtained having a diameter preferably in the range of from 1.0 to 2.0 mm, more preferably of from 1.5 to 1.7 mm.

30. The process of claim 29, wherein in (aa), a carbohydrate and/or water is/are added as pasting agent.

31. The process of claim 29 or 30, wherein the mixing in (aa) is carried out for a duration in the range of from 15 to 60 min, preferably of from 30 to 55 min, more preferably of from 40 to 50 min.

32. The process of any of claims 28 to 31, wherein in (iv), no mesopore-forming agent selected from the group consisting of polyalkylene oxides such as polyethylene oxides, polystyrene, polyacrylates, polymethacrylates, polyolefins, polyamides, and polyesters is added.

33. The process of any of claims 28 to 32, wherein in (v), the molding is dried at a temperature in the range of from 100 to 150 °C for a duration in the range of from 10 to 20 h and calcined at a temperature in the range of from 500 to 600 °C for a duration in the range of from 0.5 to 2 h.

34. The process of any of claims 28 to 33, further comprising

(vi) subjecting the molding obtained in (iv) or (v), preferably in (v), to a water-treatment;

(vii) optionally drying and/or calcining the water-treated molding,

wherein the molding obtained in (vi) or (vii), preferably in (vii), is preferably the molding according to any of claims 14 to 21.

35. The process of claim 34, wherein in (vi), the water-treatment comprises treating the molding with liquid water in an autoclave under autogenous pressure at a temperature in the range of from 100 to 200 °C, preferably of from 125 bis 175 °C, more preferably of from 140 to 150 °C for a period of from 2 to 24 hours, preferably of from 6 to 10 h.

36. The process of claim 34 or 35, wherein in (vi), the weight ratio of the molding relative to the water is in the range of from 0.02 to 0.08, preferably of from 0.03 to 0.07, more preferably of from 0.04 to 0.06.

37. The process of any of claims 34 to 35, wherein in (vii), the water-treated molding is dried at a temperature in the range of from 100 to 150 °C for a duration in the range of from 10 to 20 h and calcined at a temperature in the range of from 400 to 500 °C for a duration in the range of from 1 to 3 h.

38. The process of any of claims 28 to 37, wherein the molding is not subjected to steaming.

39. Use of the micropowder according to any of claims 1 to 13 or of the molding according to any of claims 14 to 21, as a catalyst, preferably as a catalyst for preparing propylene oxide from propene with hydrogen peroxide as oxidizing agent in acetonitrile as solvent.