

AS ORIGINALLY FILED

Silicon dioxide having mesopores and micropores

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10 The present invention relates to silicon dioxide which has mesopores and micropores. The present invention furthermore relates to processes for the preparation of such a silicon dioxide, its use, and moldings and catalysts which contain said silicon dioxide.

15 The production of silicic acids and silica gels by industrial processes is described in Ullmann, Enzyklopädie der technischen Chemie, 4th Edition, 1982, Volume 21, pages 457-463.

20 Wide-pore silica gels having a pore volume of more than 0.8 ml/g, a specific surface area of 200-400 m²/g and a pore diameter of 8-10 nm and narrow-pore silica gels having a pore volume of less than 0.5 ml/g, a specific surface area of 600-800 m²/g and a pore diameter of 2-2.5 nm have been described.

25 Nature, 359 (1992, 710 - 712) discloses aluminosilicates which have a large surface area and narrow pore size distribution and are referred to as MCM-41. For an aluminosilicate having a pore diameter of 4.5 nm, a BET surface area of more than 1000 m²/g and a pore volume of 0.79 cm³/g were found. Further aluminosilicates having pore sizes of 3 nm and 4 nm are mentioned. The X-ray diffraction pattern shows characteristic sharp bands in the range of $2\theta = 2-4^\circ$. Moreover, the aluminosilicates have a step in the nitrogen adsorption isotherm in
30 the range of $p/p_0 = 0.2 - 0.4$. The aluminosilicates are synthesized using hexadecyltrimethylammonium salts as cationic surfactants.

35 Further processes for the preparation of mesoporous molecular sieves are described in EP-A 0 670 286. Here, anionic surfactants and isopoly or heteropoly cations of specific metal oxides other than silicon dioxide are used for the synthesis.

EP-A 0 831 059 describes a mesoporous silicon dioxide and its preparation with the aid of a polymer dispersion as pore former.

A silicon dioxide having micropores and a process for its preparation are described in DE-A 197 32 865. According to this publication, a polyethyleneimine is added to a silicon dioxide precursor for the preparation of such a silicon dioxide.

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The silicon dioxides described above each have the disadvantage that they are not capable of combining the advantages of the mesopores, for example good material transport, with those of the micropores, in particular good fixation, for example of an active metal in catalysis.

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It is an object of the present invention to provide a silicon dioxide which has both mesopores and micropores and hence combines the desirable properties of excellent material transport and fixation of the active component.

15 We have found that this object is achieved by a silicon dioxide which has both mesopores and micropores.

In the novel silicon dioxide, the fraction of micropores is from 5 to 95%, preferably from 10 to 60%, in particular from 10 to 40%, of the total pore volume.

20 Accordingly, the fraction of mesopores is from 95 to 5%, preferably from 90 to 40%, in particular from 90 to 60%, of the total pore volume, the total pore volume being determined in each case by nitrogen adsorption at 77 K and a relative pressure p/p_0 of 0.98.

25 Characteristic porosity data can be determined from gas adsorption measurements, according to DIN 66131 and DIN 66134. The novel silicon dioxides have a specific surface area, expressed as the sum of micropores and mesopores, of at least 100, preferably at least 200, particularly preferably at least 300, m^2/g , the upper limit preferably being less than 500 m^2/g . The pore volume, expressed as the
30 sum of micropores and mesopores, is at least 0.2, preferably at least 0.3, in particular at least 0.4, ml/g . Mesopores are understood as meaning pores having a diameter of from 2 to 50 nm and micropores as those having pore diameters of less than 2 nm. The pore diameters and specific surface areas of the mesopores are measured by nitrogen adsorption at 77 K. The pore surface area can be calculated
35 using the BJH model (DIN 66134). The pore volume is determined at a relative pressure of $p/p_0 = 0.98$.

Preferably, the novel silicon dioxides have a maximum of the pore diameter distribution of the mesopores of at least 3 nm, preferably at least 5 nm, in particular

at least 8 nm and up to 50 nm. The pore diameter distribution can once again be determined by nitrogen adsorption at 77 K from the desorption branch of the isotherm.

5 The present invention therefore also relates to a silicon dioxide having one or more of the features:

- (i) a sum of the specific surface areas of micropores and mesopores of at least 200 m²/g;
- 10 (ii) a sum of the pore volumes of the micropores and mesopores of at least 0.2 ml/g;
- (iii) a maximum of the pore diameter distribution of the mesopores at at least 3 nm.

15 The main fraction of the mesopores preferably has a diameter of from 2 to 50 nm, particularly preferably from 4 to 30 nm, in particular from 6 to 20 nm. The main fraction relates to the main fraction of the pore volume, the pore diameter being determined by nitrogen adsorption at 77 K. Pore sizes, pore volumes and surface areas are based on calcined silicon dioxide.

20 The novel silicon dioxides have, clearly visible in the adsorption-desorption isotherm, a component of type I isotherm in the relative pressure range below 0.5 p/p₀ (nitrogen at 77 K), which is typical of the micropore fraction, and simultaneously have, above 0.5 p/p₀, a pronounced hysteresis between adsorption
25 and desorption, as is characteristic of mesoporous substances according to the BJH model (DIN 66134).

The preferred novel silicon dioxides have no characteristic step in the range of p/p₀ = 0.2 to 0.4 in the nitrogen adsorption.

30 Preferably, the novel silicon dioxides have a nitrogen adsorption isotherm at 77 K with a steep rise or a step in the range p/p₀ = 0.5 to 1.0, preferably 0.6 to 0.95. In particular, the adsorption curve shows a steep rise in the range of p/p₀ = 0.8 to 0.95, and the desorption curve a sharp decline in the range of p/p₀ = 0.7 to 0.4.
35 Preferably, both adsorption curve and desorption curve each have only one step or a steep rise.

For the X-ray diffraction patterns, Cu-K α radiation having a wavelength of 0.15406 nm was employed. The X-ray diffraction pattern of the novel silicon

dioxides has no sharp signals in the range $2\theta = < 4^\circ$, in particular $2\theta = 2$ to $< 4^\circ$. In addition, the X-ray diffraction pattern has no sharp signals or reflections in the range $2\theta = 20$ to 25° . Preferably, the X-ray diffraction pattern shows a considerable increase in the line intensity in the range $2\theta < 6^\circ$, in particular $2\theta < 4^\circ$. The largest area of the X-ray diffraction pattern is in the range $2\theta < 6^\circ$.

The novel silicon dioxides can be prepared by reacting silicon dioxide precursors in a water-containing medium which contains a polymer dispersion, the water-containing medium having a pH of < 7 . The silicon dioxides thus prepared are preferably calcined.

The molecular weights of the polymers present in the polymer dispersion are established so that a very large number of pores are obtained in the mesopore range, in order to obtain the desired surface area.

Any polymer obtainable by free radical, anionic or cationic polymerization may be used as the polymer dispersion. In general, it will be a polymer obtained by emulsion polymerization. However, polymers which are obtainable by another polymerization method, for example by suspension polymerization, can also be used. Preferably, the polymer is used in the form of a dispersion which has in particular a polymer content of from 20 to 60, in particular from 30 to 50, % by weight. This may be a primary dispersion, i.e. a dispersion as obtained in the emulsion polymerization, or a secondary dispersion, i.e. a dispersion which is obtained by subsequent dispersing of an already isolated polymer in the dispersing medium.

The dispersing medium is as a rule water. However, water-miscible organic solvents, such as alcohols and ketones, for example methanol, ethanol, n-propanol, isopropanol, n-butanol, acetone or methyl ethyl ketone, may also be present. The polymers are preferably prepared by free radical polymerization of ethylenically unsaturated monomers.

For example, particularly suitable monomers are:

ethylenically, preferably α,β -ethylenically unsaturated mono- and dicarboxylic acids, in particular those of 3 to 6 carbon atoms. Examples of these are acrylic acid, methacrylic acid, crotonic acid, fumaric acid, maleic acid, 2-methylmaleic acid or itaconic acid, as well as monoesters of ethylenically unsaturated dicarboxylic acids, such as monoalkyl maleates of C_1 - C_8 -alkanols;

vinylaromatic compounds, such as styrene, α -methylstyrene and vinyltoluenes;

linear 1-olefins, branched 1-olefins or cyclic olefins, e.g. ethene, propene, butene, isobutene, pentene, cyclopentene, hexene, cyclohexene, octene, 2,4,4-trimethyl-1-pentene, C_8 - C_{10} -olefins, 1-dodecene, C_{12} - C_{14} -olefins, octadecene, 1-eicosene (C_{20}), C_{20} - C_{24} -olefins, oligoolefins prepared by metallocene catalysis and having a terminal double bond, e.g. oligopropene, oligohexene and oligooctadecene; olefins prepared by cationic polymerization and having a high α -olefin fraction, such as polyisobutene;

butadiene;

vinyl and allyl alkyl ethers where the alkyl radical is of 1 to 40 carbon atoms, it being possible for the alkyl radical also to contain further substituents, such as hydroxyl, amino or dialkylamino or one or more alkoxyate groups, e.g. methyl vinyl ether, ethyl vinyl ether, propyl vinyl ether, isobutyl vinyl ether, 2-ethylhexyl vinyl ether, vinyl cyclohexyl ether, vinyl 4-hydroxybutyl ether, decyl vinyl ether, dodecyl vinyl ether, octadecyl vinyl ether, 2-(diethylamino)ethyl vinyl ether, 2-(di-n-butylamino)ethyl vinyl ether or methyldiglycol vinyl ether, and the corresponding allyl ethers and mixtures thereof;

acrylamides and alkyl-substituted acrylamides, e.g. acrylamide, methacrylamide, N-tert-butylacrylamide or N-methyl(meth)acrylamide;

sulfo-containing monomers, e.g. allylsulfonic acid, methallylsulfonic acid, styrene sulfonate, vinylsulfonic acid, allyloxybenzenesulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid, the corresponding alkali and ammonium salts thereof and mixtures thereof;

C_1 - to C_8 -alkyl esters or hydroxy- C_1 - to C_4 -alkyl esters of C_3 - to C_6 -mono- or dicarboxylic acids (see above), in particular of acrylic acid, methacrylic acid or maleic acid, or esters of C_1 - to C_{18} -alcohols, alkoxylated with from 2 to 50 mol of ethylene oxide, propylene oxide, butylene oxide or mixtures thereof, with the stated acids, e.g. methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, isopropyl (meth)acrylate, butyl (meth)acrylate, hexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, butynediol 1,4-monoacrylate, dibutyl maleate, ethyldiglycol

acrylate, methylpolyglycol acrylate (11 EO), (meth)acrylic esters of C₁₃/C₁₅-oxo alcohol reacted with 3, 5, 7, 10 or 30 mol of ethylene oxide, or mixtures thereof;

alkylaminoalkyl (meth)acrylates or alkylaminoalkyl-(meth)acrylamides, e.g. 2-
 5 (N,N-dimethylamino)ethyl (meth)acrylate, 3-(N,N-dimethylamino)propyl (meth)-
 acrylate, 2-(N,N,N-trimethylammonium)ethyl (meth)acrylate chloride, 2-
 dimethylaminoethyl(meth)acrylamide, 3-dimethylaminopropyl(meth)acrylamide or
 3-trimethylammoniumpropyl(meth)acrylamide chloride, and their quaternization
 10 products, for example with dimethyl sulfate, diethyl sulfate or other alkylating
 agents, vinyl and allyl esters of C₁- to C₃₀-monocarboxylic acids, such as vinyl
 formate, vinyl 2-ethylhexanoate, vinyl nonanoate, vinyl decanoate, vinyl pivalate,
 vinyl palmitate, vinyl stearate or vinyl laurate.

The following may be mentioned as further monomers:

15 vinylformamide, N-vinyl-N-methylformamide, styrene, 2-methylstyrene, 3-
 methylstyrene, butadiene, N-vinylpyrrolidone, N-vinylimidazole, 1-vinyl-2-
 methylimidazole, 1-vinyl-2-methylimidazoline, N-vinylcaprolactam, acrylonitrile,
 methacrylonitrile, allyl alcohol, 2-vinylpyridine, 4-vinylpyridine, diallyl-
 20 dimethylammonium chloride, vinylidene chloride, vinyl chloride, acrolein,
 methacrolein and vinylcarbazole and mixtures thereof; quaternization products of
 said N-vinylimidazole monomers with dimethyl sulfate, diethyl sulfate or other
 alkylating agents.

25 Preferred monomers are esters of acrylic acid and methacrylic acid, vinylaromatic
 compounds, butadiene, vinyl esters, (meth)acrylonitrile and (meth)acrylamides.

Particularly preferred monomers are methyl acrylate, ethyl acrylates, butyl
 acrylates, 2-ethylhexyl acrylate, methyl methacrylate, butyl methacrylate,
 30 hydroxyethyl acrylates, hydroxypropyl acrylate, hydroxybutyl acrylate,
 hydroxyethyl methacrylate, styrene, butadiene, vinyl acetate, acrylonitrile,
 methacrylonitrile, acrylamide, methacrylamide and/or N-butylacrylamide.

The polymers can be prepared by conventional polymerization processes, for
 35 example by free radical mass, emulsion, suspension, dispersion, solution and
 precipitation polymerization. Said polymerization processes are preferably carried
 out in the absence of oxygen, preferably in a stream of nitrogen. For all
 polymerization methods, the conventional apparatuses are used, for example stirred
 kettles, stirred kettle cascades, autoclaves, tube reactors and kneaders. The

emulsion, precipitation or suspension polymerization method is preferably used. The free radical emulsion polymerization method in an aqueous medium is particularly preferred.

5 When the aqueous emulsion polymerization is employed, polymers having a weight average molecular weight of from 1000 to 2,000,000, preferably from 5000 to 500,000, are obtained. The K values are in general from 15 to 150 (1% strength by weight in dimethylformamide). The mean particle size (determined by means of light scattering (autosizer)) is from 20 to 1000 nm, preferably from 30 to 700
10 nm, particularly preferably from 40 to 400 nm. The dispersion may have a monomodal or polymodal particle size distribution. The emulsion polymerization can be carried out such that the solids volume content is from 10 to 70%, preferably from 20 to 60%.

15 The polymerization is preferably carried out in the presence of compounds forming free radicals (initiators). Preferably from 0.05 to 15, particularly preferably from 0.2 to 8, % by weight, based on the monomers used in the polymerization, of these compounds are required.

20 Suitable polymerization initiators are the known initiators described in EP-A 0 831 059, for example peroxides, hydroperoxides, peroxodisulfates, percarbonates, peroxyesters, hydrogen peroxide and azo compounds. Examples of initiators which may be water-soluble or water-insoluble are hydrogen peroxide, dibenzoyl peroxide, dicyclohexyl peroxodicarbonate, dilauroyl peroxide, methyl ethyl ketone
25 peroxide, di-tert-butyl peroxide, acetylacetone peroxide, tert-butyl hydroperoxide, cumyl hydroperoxide, tert-butyl perneodecanoate, tert-amyl perpivalate, tert-butyl perpivalate, tert-butyl perneohexanoate, tert-butyl per-2-ethylhexanoate, tert-butyl perbenzoate, lithium, sodium, potassium and ammonium peroxodisulfate, azobisisobutyronitrile, 2,2'-azobis(2-amidinopropane) dihydrochloride 2-
30 (carbamoylazo)isobutyronitrile and 4,4'-azobis(4-cyanovaleric acid). The known redox initiator systems, too, can be used as polymerization initiators.

The initiators can be used alone or as a mixture with one another, for example mixtures of hydrogen peroxide and sodium peroxodisulfate. For polymerization in
35 an aqueous medium, water-soluble initiators are preferably used.

In order to prepare polymers having a low average molecular weight, it is often expedient to carry out the copolymerization in the presence of regulators. Conventional regulators may be used for this purpose, for example organic

compounds containing SH groups, such as 2-mercaptoethanol, 2-mercaptopropanol, mercaptoacetic acid, tert-butyl mercaptan, n-octyl mercaptan, n-dodecyl mercaptan and tert-dodecyl mercaptan, C₁- to C₄-aldehydes, such as formaldehyde, acetaldehyde and propionaldehyde, hydroxylammonium salts, such as hydroxylammonium sulfate, formic acid, sodium bisulfite and isopropanol. The polymerization regulators are used in general in amounts of from 0.1 to 10% by weight, based on the monomers.

To prepare relatively high molecular weight or crosslinked copolymers, it is often expedient to carry out the polymerization in the presence of crosslinking agents. Such crosslinking agents are compounds having two or more ethylenically unsaturated groups, for example diacrylates or dimethacrylates of at least dihydric saturated alcohols, e.g. ethylene glycol diacrylate, ethylene glycol dimethacrylate, 1,2-propylene glycol diacrylate, 1,2-propylene glycol dimethacrylate, neopentylglycol dimethacrylate, 3-methylpentanediol diacrylate and 3-methylpentanediol dimethacrylate. The acrylates and methacrylates of alcohols having more than 2 OH groups may also be used as crosslinking agents, e.g. trimethylolpropane triacrylate or trimethylolpropane trimethacrylate. A further class of crosslinking agents comprises diacrylates or dimethacrylates of polyethylene glycols or polypropylene glycols having molecular weights in each case of from 200 to 9000.

In addition to the homopolymers of ethylene oxide or propylene oxide, it is also possible to use block copolymers of ethylene oxide and propylene oxide or copolymers of ethylene oxide and propylene oxide which contain the ethylene oxide and propylene oxide units randomly distributed. Furthermore, the oligomers of ethylene oxide or of propylene oxide are suitable for the preparation of the crosslinking agents, e.g. diethylene glycol diacrylate, diethylene glycol dimethacrylate, triethylene glycol diacrylate, triethylene glycol dimethacrylate, tetraethylene glycol diacrylate and/or tetraethylene glycol dimethacrylate.

Further suitable crosslinking agents are vinyl acrylate, vinyl methacrylate, vinyl itaconate, divinyl adipate, butanediol divinyl ether, trimethylolpropane trivinyl ether, allyl acrylate, allyl methacrylate, pentaallylsucrose, methylenebis(meth)acrylamide, divinylethyleneurea, divinylpropyleneurea, divinylbenzene, divinylidioxane, triallyl cyanurate, tetraallylsilane, tetravinylsilane and bis- and polyacryloylsiloxanes (e.g. Tegomere[®] from Th. Goldschmidt AG). The crosslinking agents are preferably used in amounts of from 0.05 to 50,

preferably from 0.1 to 20, in particular from 0.5 to 10, % by weight, based on the monomers to be polymerized.

If the emulsion, precipitation, suspension or dispersion polymerization method is used, it may be advantageous to stabilize the polymer droplets or polymer particles by means of surfactants. Emulsifiers or protective colloids are typically used for this purpose. Anionic, nonionic, cationic and amphoteric emulsifiers are suitable. Anionic emulsifiers, for example alkylbenzenesulfonic acids, sulfonated fatty acids, sulfosuccinates, fatty alcohol sulfates, alkylphenol sulfates and fatty alcohol ether sulfates, are preferred. Nonionic emulsifiers which may be used are, for example, alkylphenol ethoxylates, primary alcohol ethoxylates, fatty acid ethoxylates, alkanolamide ethoxylates, fatty amine ethoxylates, EO/PO block copolymers and alkylpolyglucosides. For example, the following may be used as cationic or amphoteric emulsifiers: quaternized aminoalkoxylates, alkylbetaines, alkylamidobetaines and sulfobetaines. Long-chain quaternary amines, for example fatty amines quaternized with dimethyl sulfate, are also suitable.

Protective colloids are, for example, cellulose derivatives, polyethylene glycol, polypropylene glycol, copolymers of ethylene glycol and propylene glycol, polyvinyl acetate, polyvinyl alcohol, polyvinyl ether, starch and starch derivatives, dextran, polyvinylpyrrolidone, polyvinylpyridine, polyethyleneimine, polyvinylamine, polyvinylformamide, polyvinylimidazole, polyvinylsuccinimide, polyvinyl-2-methylsuccinimide, polyvinyl-1,3-oxazolid-2-one, polyvinyl-2-methylimidazoline and copolymers containing acrylic acid, methacrylic acid, maleic acid or maleic anhydride. The emulsifiers or protective colloids are usually used in concentrations of from 0.05 to 20% by weight, based on the monomers.

If polymerization is effected in aqueous emulsion or dilution, the monomers and emulsifiers may be wholly or partly neutralized before or during the polymerization by means of conventional, inorganic or organic bases or acids. Suitable bases are, for example, alkali metal or alkaline earth metal compounds, such as sodium, potassium or calcium hydroxide, sodium carbonate, ammonia and primary, secondary or tertiary amines, such as di- or triethanolamine. Suitable acids are, for example, hydrochloric acid, sulfuric acid, phosphoric acid, formic acid and acetic acid.

Cationic aqueous polymer dispersions which have been stabilized with cationic emulsifiers and/or cationic auxiliary monomers (emulsifiers or α,β -ethylenically unsaturated monomers which contain quaternary amine or ammonium structures)

are particularly preferably used. These emulsion polymers are preferably prepared using free radical formers containing cationic groups.

5 Particularly preferred monomers are methyl methacrylate, styrene, n-butyl acrylate, butanediol diacrylate and N,N-dimethylaminoethyl methacrylate quaternized with diethyl sulfate. Preferably, the polymer dispersion contains polymers having basic building blocks comprising methyl methacrylate, butanediol diacrylate, and/or dimethylaminoethyl methacrylate quaternized with diethyl sulfate.

10 The polymerization can be carried out in a conventional manner by a large number of different methods, continuously or batchwise. If the polymer is prepared by a solution, precipitation or suspension polymerization method in a steam-volatile solvent or solvent mixture, the solvent can be separated off by passing in steam, in order thus to obtain an aqueous solution or dispersion. The polymer can also be
15 isolated from the organic diluent by a drying process.

The polymer may be, for example, a rubber, such as an epichlorohydrin rubber, ethylene/vinyl acetate rubber, chlorosulfinated polyethylene rubber, silicone
20 rubber, polyether rubber, diene rubber, such as butadiene rubber, acrylate rubber, ethylene/propylene rubber, ethylene/propylene/diene rubber or butyl rubber or similar rubber.

In the case of secondary dispersions, polymers not prepared by free radical polymerization, e.g. polysiloxanes, polyurethanes and polyesters, can also be used.
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The glass transition temperature of the polymer dispersions used according to the invention (measured in the dry state by means of DSC) is from -50 to +150°C, preferably from 0 to 110°C.

30 The concentration of the polymer in the reaction medium is preferably from 0.05 to 20, particularly preferably from 0.25 to 10, in particular from 0.5 to 10, especially from 0.5 to 5, % by weight, based on the total reaction mixture. Particularly preferably, the polymer dispersion is present in the water-containing or aqueous phase in a two-phase reaction medium.

35 The reaction medium used may be any suitable water-containing reaction medium. For example, water may be used as the reaction medium. In addition, a mixture of water with a water-soluble organic auxiliary solvent, such as a lower alcohol, such as ethanol or isopropanol, may be used. The reaction can also be carried out in a

two-phase reaction medium which consists of an aqueous phase and an organic phase which is immiscible or only slightly miscible with water. The organic phase should be inert with respect to the reaction. The water-containing reaction medium or the two-phase mixture may be agitated, in particular stirred, during the reaction, but it is also possible to carry out a reaction in unagitated phase, in particular at the phase boundary of a two-phase system. If the reaction is carried out at a stationary interface, the silicon dioxide can be obtained in the form of thin films or layers. The oxide films or oxide layers thus obtained can be used in membrane, separation and purification processes or in applications for information storage. Corresponding films or layers may furthermore be suitable for electronic, optical or electrooptical applications. The membranes can furthermore be used for catalytic reactions in membrane reactors or in reactive distillations.

The silicon dioxide precursors used may be any suitable compounds which give silicon dioxide as a result of a physical or chemical treatment. Examples are organic silicon compounds, in particular hydrolyzable organic silicon compounds, such as alcoholates or chelates. It is also possible to use the silicon dioxide precursor in the form of an organic silicon compound, preferably of a soluble salt or colloid, as well as in the form of waterglass or pyrogenic silica.

Preferably, organic silicon compounds in the form of tetraalcoholates, such as tetramethoxysilicon or tetraethoxysilicon, are used. The tetraalkoxysilicon compound, in particular C₁-C₄-alkoxy compound, can be initially taken in an organic solvent and reacted at the phase boundary in a two-phase reaction medium. The novel silicon dioxide forms at the phase boundary of the immiscible phases. When the reaction medium is mixed, in particular stirred, an emulsion either of the organic solvent in water or of water in the organic solvent forms. By varying the intensity of mixing or the stirrer speed, during mechanical stirring, the type and size of the resulting silicon dioxide particles can be determined, so that silicon dioxide moldings are obtainable. If a substrate is introduced into the region of the boundary layer between two different phases as the reaction medium, deposition of the novel silicon dioxide on this substrate can occur. For example, the substrate may be an inert porous substrate, such as a porous glass, alumina, silica gel or clay, ceramic, metal or a metal packing, as used, for example, for static mixers. This inert substrate can thus be coated or impregnated with the novel silicon dioxide, giving composite materials which have good mechanical stability, in particular in comparison with substrate-free mesoporous oxide moldings.

The preparation of moldings from the novel silicon dioxide can also be carried out after the reaction. Novel silicon dioxide obtained in the reaction, in particular in powder form, is brought into the form of the desired molding by suitable measures. Suitable methods are known; for example, the novel silicon dioxide can be mixed
5 with a binder and compressed to give pellets. Shaping by extrusion is also possible.

The reaction medium may contain further additives, for example metal ions or noble metal ions. For example, ions of the elements Al, B or Ge or of groups IIIa,
10 IIb, IVb, Vb and VIb of the Periodic Table of the Elements, Be, Sn, Pb, Bi, Cu, Fe, Co, Ni, Ce, Mn or mixtures thereof are suitable. In the case of two-phase reaction media, the metal ions may be present in one of the two phases or in both phases. Consequently, it is possible to introduce catalytically active metals into the novel silicon dioxide or moldings prepared therefrom, for example in the case of catalyst
15 applications. It is also possible, for example for biotechnological applications, to introduce enzymes into the water-containing reaction medium or the aqueous phase of a two-phase reaction medium, which are then also incorporated by condensation. The inclusion of pharmacologically active substances, such as pharmaceutical active substances, is also possible owing to the mild reaction
20 conditions. It is thus possible to prepare novel silicon dioxides or corresponding moldings which release a pharmaceutical active substance slowly in a specific application.

Furthermore, pigments can be introduced into the reaction medium and are then
25 present in the novel silicon dioxide or moldings thereof. Thus, it is possible to prepare colored silicon dioxide or moldings thereof.

The reaction is preferably carried out at from -10 to +150°C, preferably from 10 to 90°C, particularly preferably from 20 to 65°C. The reaction can be carried out at
30 atmospheric pressure, reduced pressure or superatmospheric pressure, such as from 0.4 to 300 bar. The reaction is preferably carried out at atmospheric pressure.

The novel process must be carried out in the acidic pH range, i.e. at a pH of < 7. A pH of from 5 to 1 is preferably employed. Acidification can be carried out by
35 means of all acids, for example mineral acids, such as HCl, HNO₃, H₂SO₄ and HF, or heteropoly acids, such as heteropolytungstates.

In addition, however, SiO₂ can also be dissolved directly with HF and hence per se an acidic medium obtained, as described in WO 97/16374.

The novel silicon dioxides obtained after the reaction or moldings prepared therefrom can, according to the invention, be calcined, for example in order to use them as catalysts or catalyst supports. According to the invention, the calcination is preferably carried out at from 300 to 600°C, preferably from 400 to 450°C. The calcination period may be from 0.5 to 20, preferably from 2 to 8, hours. If required, a drying step may be introduced before the calcination, in order to obtain a dry silicon dioxide. The silicon dioxides used according to the invention for the calcination have only a small amount of polymer from the polymer dispersion. Preferably, the amount of polymer dispersion in the dried silicon dioxide before the calcination is from 5 to 200, particularly preferably from 30 to 150, % by weight, based on the total mass of silicon dioxide and polymer.

The novel silicon dioxides or moldings prepared therefrom or therewith or coated therewith can be used in a large number of applications. The oxide films or layers formed in the synthesis in an unagitated two-phase reaction medium can be used as self-supporting membranes.

Moreover, the novel silicon dioxide or moldings prepared therefrom can be used as catalysts or catalyst supports. The catalysts contain the novel silicon dioxide as a substrate or as active substance. Examples of suitable catalytic reactions are the introduction of oxy functional groups in hydrocarbons, the oxidation of olefins to oxiranes, the alkylation of aromatics, hydrogenations, dehydrogenations, hydrations, dehydrations, isomerizations, addition and elimination reactions, nucleophilic and electrophilic substitution reactions, dehydrocyclizations, hydroxylations of hetero atoms and aromatics, epoxide-aldehyde rearrangements, aminations of monomeric and oligomeric olefins, condensation reactions of the aldol type, polymerization reactions, esterifications and etherification reactions, as well as catalytic reactions of exit gases and stack gases and removal of oxides of nitrogen. The use for storing and slowly releasing drugs as well as for taking up pigments, which are then present in the mesoporous oxide molding, for example in encapsulated form, has been described above. The use as sorbents and for the production of oxide ceramics or the use in the separation of substances are also possible. The surface characteristics of the novel silicon dioxides or moldings thereof can be controlled by the type of dispersion used. The dispersion can serve as a kind of die or mold for the pore structure to be obtained.

Example 1

209 g of tetraethoxysilane (from Merck), 300 g of ethanol and 61 g of isopropanol
 5 were mixed in a 2 l four-necked flask with stirring. A mixture of 50 g of the
 polymer dispersion below in 650 g of demineralized water with 7.5 g of
 hydrochloric acid (10% by weight) was added dropwise to this mixture. The
 resulting white suspension was stirred for one hour at room temperature. The
 suspension was then evaporated down in a rotary evaporator at 60°C under reduced
 10 pressure from a water jet pump. The dried material was then calcined for 5 hours
 at 500°C in air. 56 g of calcined product were obtained.

Properties of polymer dispersions used

15
 Monomers: 90% by weight of methyl methacrylate
 5% by weight of Quat 311 (dimethylamino-
 ethylmethacrylamide, quaternized with diethyl sulfate)
 5% by weight of butanediol diacrylate
 20 Others: 1.0% by weight of azo initiator V50 (from Wako
 Chemicals GmbH)
 10.0% by weight of Lipamin OK (cationic emulsifier)
 Solids content: 30% by weight
 Particle size: 100-110 nm

25
 The sorption curve shown in Figure 1 was measured by means of nitrogen
 adsorption at 77 K. The curve marked with crosses reproduces the adsorption, and
 that marked with asterisks reproduces the desorption. The abscissa gives the
 cumulative adsorbed gas volume at standard temperature and pressure (V). A
 30 typical hysteresis in the relative pressure range of $p/p_0 > 0.4$ was obtained. Using
 the BJH model, a surface area of the mesopores of 330 m²/g was determined
 therefrom for the pores in the pore diameter range from about 2 to 200 nm. The
 corresponding volume of the mesopores was 0.29 ml/g, and the total volume of
 micropores and mesopores, determined at $p/p_0 = 0.98$, was 0.375 ml/g. The most
 35 frequent diameter of the mesopores, calculated from the desorption branch of the
 hysteresis, was 3.6 nm. The surface area calculated according to Langmuir in the
 relative pressure range up to 0.2 p/p_0 was 720 m²/g.

Example 2

This Example describes the preparation, according to the invention, of a titanium-containing silicon dioxide. For this purpose, 7.4 g of tetraisopropyl orthotitanate, 209 g of tetraethoxysilane (from Merck), 300 g of ethanol and 61 g of isopropanol were mixed in a 2 l four-necked flask with stirring. A mixture of 50 g of the above polymer dispersion in 650 g of demineralized water with 7.5 g of hydrochloric acid (10% by weight) was added dropwise to this mixture. The resulting white suspension was stirred for one hour at room temperature. The suspension was then evaporated down in a rotary evaporator at 60°C under reduced pressure from a water jet pump. The dried material was then calcined for 5 hours at 500°C in air. 63 g of product were obtained. According to wet chemical analysis, the material contained 2.1% by weight of titanium. An ESCA analysis of the Ti-2p lines showed a titanium distribution of 17% at a bond energy of 458.2 eV and 83% at a bond energy of 460 eV, corresponding to the proportions of octahedrally and tetrahedrally coordinated titanium, respectively.

By means of nitrogen adsorption at 77 K, the typical sorption curve shown in Figure 1 was once again observed. Using the BJH model, a surface area of the mesopores of 243 m²/g was determined therefrom for the pores in the pore diameter range from about 2 to 200 nm. The corresponding volume of the mesopores was 0.24 ml/g, and the total volume of micropores and mesopores, determined at $p/p_0 = 0.98$, was 0.34 ml/g. The most frequent diameter of the mesopores, calculated from the desorption branch of the hysteresis, was 4.1 nm. The surface area calculated according to Langmuir in the relative pressure range up to 0.2 p/p_0 was 633 m²/g.

In a microgravimetric determination of the sorption capacity for propylene, a capacity of 7.9% by weight was measured at room temperature (20°C) and a propene partial pressure of 699 mbar.

In an analogous manner, the sorption capacity for propylene oxide at 20°C and 199 mbar was determined microgravimetrically to be 24.6% by weight.

Example 3

Use of the novel titanium-containing silicon dioxide from Example 2 for the epoxidation of propene with hydrogen peroxide.

45 g of methanol were initially taken in a glass pressure autoclave, and 0.5 g of catalyst from Example 2 was suspended with stirring. After closing, 10.25 g of propene were forced in at 30°C/2.5 bar and 17.2 g of a 30% strength hydrogen peroxide solution were metered in by means of a pump. After an operating time of 5 hours, the autoclave was let down and the liquid phase was analyzed by means of GC. The discharge contained 0.05% by weight of propylene oxide, corresponding to 1.9 turnovers, based on the total amount of titanium used in the catalyst. Other oxidation products of propene apart from propylene oxide were not found.

10 **Example 4**

This Example describes the preparation, according to the invention, of an iron-containing silicon dioxide. For this purpose, 209 g of tetraethoxysilane (from Merck), 300 g of ethanol and 61 g of isopropanol were mixed in a 2 l four-necked flask with stirring. A mixture of 50 g of polymer dispersion in 650 g of demineralized water, with the addition of 7.5 g of hydrochloric acid (10% by weight) and 3.2 g of iron(II) sulfate, was added dropwise to this mixture. The resulting brown-yellow suspension was stirred for one hour at room temperature. The suspension was then evaporated down in a rotary evaporator at 60°C under reduced pressure from a water jet pump. The dried material was then calcined for 5 hours at 500°C in air. 60 g of product were obtained. According to wet chemical analysis, the material contained 1.1% by weight of iron.

By means of nitrogen adsorption at 77 K, the typical sorption curve shown in Figure 1 was once again observed. Using the BJH model, a surface area of the mesopores of 215 m²/g was determined therefrom for the pores in the pore diameter range from about 2 to 200 nm. The corresponding volume of the mesopores was 0.21 ml/g. The surface area calculated according to Langmuir in the relative pressure range up to 0.2 p/p₀ was 444 m²/g.

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Example 5

Use of the novel silicon dioxide according to Example 4 with decomposition of hydrogen peroxide.

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In each case 10 g of novel catalyst from Example 1 (Si-MPO) and from Example 4 (Fe-Si-MPO) were reacted with 100 g of 30% strength hydrogen peroxide solution in a glass autoclave. The iron-containing material from Example 4 exhibited its

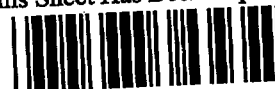
excellent properties as a deperoxidation catalyst. The results are compared in the Table below.

Operating time [hours]	Catalyst	
	Example 4 [Fe-Si-MPO] Content of H ₂ O ₂ [% by weight]	Example 1 [Si-MPO] Content of H ₂ O ₂ [% by weight]
0	30.7	30.7
1	0.6	29.8
2	0.5	29.7
3	0.5	29.6

**We claim:**

- 5
1. A silicon dioxide which has mesopores and micropores.
 2. A silicon dioxide as claimed in claim 1, wherein the fraction of mesopores is from 95 to 5% and the fraction of micropores is from 5 to 95%, based in
10 each case on the overall sum of mesopores and micropores in the silicon dioxide.
 3. A silicon dioxide as claimed in claim 1 or 2, having one or more of the features:
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 - (i) a sum of the specific surface areas of micropores and mesopores of at least 200 m²/g;
 - (ii) a sum of the pore volumes of micropores and mesopores of at least 0.2 ml/g;
 - 20 (iii) a maximum of the pore diameter distribution of the mesopores at at least 3 nm.
 4. A process for the preparation of a silicon dioxide which has micropores and mesopores by bringing at least one silicon dioxide precursor into contact
25 with a polymer dispersion in a water-containing medium which contains a polymer dispersion, wherein the water-containing medium has a pH of < 7.
 5. A process as claimed in claim 4, wherein the polymer dispersion is cationic.
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 6. A process as claimed in claim 4 or 5, wherein the polymer dispersion contains at least one polymer which contains basic building blocks derived from dimethylaminoethyl methacrylate quaternized with methyl methacrylate, butanediol diacrylate and/or diethyl sulfate.
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 7. A process as claimed in any of claims 4 to 6, wherein the silicon dioxide precursor is used in the form of an organic silicon compound, of a silicon salt, of waterglass or of pyrogenic silica.

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8. A silicon dioxide preparable by bringing a silicon dioxide precursor into contact with a polymer dispersion in a water-containing medium which has a pH of < 7 .
- 5 9. A silicon dioxide as claimed in any of claims 1 to 3 or 8, which additionally contains at least one element selected from the group consisting of Al, B, Ge, groups IIIa, VIIIa, Ib, IIb, IVa, IVb, Va, Vb, VIa and VIb of the Periodic Table of the Elements, Be, Sn, Pb, Bi, Cu, Fe, Co, Ni, Ce, Mn, Re and mixtures of two or more thereof, pharmacologically active substances, 10 enzymes, pigments and mixtures of two or more thereof.
10. The use of a silicon dioxide as claimed in any of claims 1 to 3, 8 or 9 or of a silicon dioxide prepared by a process as claimed in any of claims 4 to 7, for the preparation of moldings or as a catalyst or carrier for catalysts or 15 pharmacologically active substances, enzymes or pigments.
11. A molding containing at least one, coated with at least one or consisting of at least one silicon dioxide as claimed in any of claims 1 to 3, 8 or 9 or a silicon dioxide prepared by a process as claimed in any of claims 4 to 7. 20
12. A catalyst containing at least one silicon dioxide as claimed in any of claims 1 to 3, 8 or 9 or of a silicon dioxide prepared by a process as claimed in any of claims 4 to 7.

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