

Granules based on pyrogenically prepared
silicon dioxide, method for their preparation and
use thereof

- 5 The invention relates to granules based on pyrogenically prepared silicon dioxide, the method for their preparation and the use thereof as catalyst supports.

The preparation of pyrogenic silicas or silicon dioxides
10 from SiCl_4 by means of high-temperature-or flame hydrolysis is known (Ullmanns Enzyklopädie der technischen Chemie, 4th Edition, Volume 21, page 464 (1982)).

Pyrogenic silicon dioxides are distinguished by having
15 extremely fine particles, high specific surface (BET), very high purity, spherical particle shape and the absence of pores. On account of these properties pyrogenically prepared silicon dioxides are attracting increasing interest as supports for catalysts (Dr. Koth et al., Chem.
20 Ing. Techn. 52, 628 (1980)). For this application the pyrogenically prepared silicon dioxide is shaped by mechanical means, for example, tableting machines.

The shaping of pyrogenically prepared silicon dioxide into
25 sprayed granules also by means of spray drying, to obtain a starting material for sintered ceramic materials, is also known (DE-A 36 11 449).

It is also known that silicon dioxide pyrogenically
30 prepared in an electric arc may be shaped by means of spray drying into sprayed granules, which can be used as adsorption media or else as catalyst supports (DE-A 12 09 108).

35 The subjection of pyrogenically prepared silicon dioxide to a gel process and the subsequent shaping into granules by means of spray drying is also known. These granules, after



coating with chromium oxide, are used in the polymerisation of ethylene (EP-A 0 050 902, US-A 4,386,016).

Furthermore, the use of precipitated silicon dioxide as a catalyst support for the catalytic polymerisation of olefins is known (WO 91/09881).

The known sprayed granules of pyrogenically prepared silicon dioxides have the disadvantage that they are not optimally suitable for use as catalyst supports, for example, in the production of polyethylene.

The object was therefore the development from pyrogenically prepared silicon dioxide of sprayed granules which can be used as catalyst supports in the production of polyethylene.

The present invention provides granules based on pyrogenically prepared silicon dioxide and having the following physicochemical properties:

Average grain size:	10 to 120 μm
BET surface area:	40 to 400 m^2/g
Pore volume:	0.5 to 2.5 ml/g
25 Pore size distribution:	less than 5 % of the total pore volume exists of pores with a diameter < 5 nm, rest meso- and macropores
pH value:	3.6 to 8.5
30 Tapped density:	220 to 700 g/l

The granular material according to the invention can be prepared by dispersing pyrogenically prepared silicon dioxide in water, spray drying it and heating the granules obtained at a temperature of from 150 to 1,100°C for a period of 1 to 8 h.



The invention also provides granules based on pyrogenically prepared silicon dioxide and having the following physicochemical properties:

- 5 Average grain size: 10 to 120 μm
BET surface area: 40 to 400 m^2/g
Pore volume: 0.5 to 2.5 ml/g
Pore size distribution: less than 5 % of the total pore
10 volume exists of pores with a
diameter < 5 nm, rest meso- and
macropores
pH value: 3.6 to 8.5
Tapped density: 220 to 700 g/l

- 15 The granular material according to the invention can be prepared by dispersing pyrogenically prepared silicon dioxide in water, spray drying it and silanising the granules obtained. Halosilanes, alkoxysilanes, silazanes and/or siloxanes can be used for the silanisation.

- 20 The following substances in particular can be used as halosilanes:

- 25 Haloorganosilanes of the type $\text{X}_3 \text{Si}(\text{C}_n\text{H}_{2n+1})$ X = Cl, Br
n = 1 to 20

- Haloorganosilanes of the type $\text{X}_2 (\text{R}')\text{Si}(\text{C}_n\text{H}_{2n+1})$ X = Cl, Br
R' = alkyl
n = 1 to 20

- 30 Haloorganosilanes of the type $\text{X}(\text{R}')_2 \text{Si}(\text{C}_n\text{H}_{2n+1})$ X = Cl, Br
R' = alkyl
n = 1 to 20

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Haloorganosilanes of the type $X_3 Si(CH_2)_m-R'$

X = Cl, Br

m = 0.1 to 20

R' = alkyl, aryl (for example, $-C_6H_5$)

- 5 $-C_4F_9$, $-OCF_2-CHF-CF_3$, $-C_6F_{13}$, $-O-CF_2-CHF_2$
 $-NH_2$, $-N_3$, $-SCN$, $-CH=CH_2$,
 $-OOC(CH_3)C=CH_2$
 $-OCH_2-CH(O)CH_2$
 $-NH-CO-N-CO-(CH_2)_5$
10 $-NH-COO-CH_3$, $-NH-COO-CH_2-CH_3$, $-NH-(CH_2)_3Si(OR)_3$
 $-S_x-(CH_2)_3Si(OR)_3$

Haloorganosilanes of the type $(R)_X Si(CH_2)_m-R'$

X = Cl, Br

15 R = alkyl

m = 0.1 to 20

R' = alkyl, aryl (for example, $-C_6H_5$)

- $-C_4F_9$, $-OCF_2-CHF-CF_3$, $-C_6F_{13}$, $-O-CF_2-CHF_2$
 $-NH_2$, $-N_3$, $-SCN$, $-CH=CH_2$,
20 $-OOC(CH_3)C=CH_2$
 $-OCH_2-CH(O)CH_2$
 $-NH-CO-N-CO-(CH_2)_5$
 $-NH-COO-CH_3$, $-NH-COO-CH_2-CH_3$, $-NH-(CH_2)_3Si(OR)_3$
 $-S_x-(CH_2)_3Si(OR)_3$

25

Haloorganosilanes of the type $(R)_2 X Si(CH_2)_m-R'$

X = Cl, Br

R = alkyl

m = 0.1 to 20

30 R' = alkyl, aryl (for example, $-C_6H_5$)

- $-C_4F_9$, $-OCF_2-CHF-CF_3$, $-C_6F_{13}$, $-O-CF_2-CHF_2$
 $-NH_2$, $-N_3$, $-SCN$, $-CH=CH_2$,
 $-OOC(CH_3)C=CH_2$
 $-OCH_2-CH(O)CH_2$
35 $-NH-CO-N-CO-(CH_2)_5$
 $-NH-COO-CH_3$, $-NH-COO-CH_2-CH_3$, $-NH-(CH_2)_3Si(OR)_3$
 $-S_x-(CH_2)_3Si(OR)_3$



The following substances in particular can be used as
alkoxysilanes:

- 5 Organosilanes of the type $(RO)_3 Si(C_nH_{2n+1})$ $R = \text{alkyl}$
 $n = 1 \text{ to } 20$
- Organosilanes of the type $R'_x (RO)_y Si(C_nH_{2n+1})$ $R = \text{alkyl}$
 $R' = \text{alkyl}$
 $n = 1 \text{ to } 20$
10 $x+y = 3$
 $x = 1, 2$
 $y = 1, 2$

- Organosilanes of the type $(RO)_3 Si(CH_2)_m-R'$
- 15 $R = \text{alkyl}$
 $m = 0.1 \text{ to } 20$
 $R' = \text{alkyl, aryl (for example, } -C_6H_5)$
 $-C_4F_9, -OCF_2-CHF-CF_3, -C_6F_{13}, -O-CF_2-CHF_2$
 $-NH_2, -N_3, -SCN, -CH=CH_2,$
- 20 $-OOC(CH_3)C = CH_2$
 $-OCH_2-CH(O)CH_2$
 $-NH-CO-N-CO-(CH_2)_5$
 $-NH-COO-CH_3, -NH-COO-CH_2-CH_3, -NH-(CH_2)_3Si(OR)_3$
 $-S_x-(CH_2)_3Si(OR)_3$

- 25 Organosilanes of the type $(R'')_x (RO)_y Si(CH_2)_m-R'$
 $R'' = \text{alkyl}$ $x+y = 2$
 $x = 1, 2$
 $y = 1, 2$

- 30 $R' = \text{alkyl, aryl (for example, } -C_6H_5)$
 $-C_4F_9, -OCF_2-CHF-CF_3, -C_6F_{13}, -O-CF_2-CHF_2$
 $-NH_2, -N_3, -SCN, -CH=CH_2,$
 $-OOC(CH_3)C = CH_2$
 $-OCH_2-CH(O)CH_2$
- 35 $-NH-CO-N-CO-(CH_2)_5$
 $-NH-COO-CH_3, -NH-COO-CH_2-CH_3, -NH-(CH_2)_3Si(OR)_3$
 $-S_x-(CH_2)_3Si(OR)_3$



Preferably the silane Si 108 $[(CH_3O)_3Si-C_8H_{17}]$,
trimethoxyoctylsilane, is used as silanising agent.

The following substances in particular can be used as
5 silazanes:

silazanes of the type $R'R_2Si-N-SiR_2R'$



10

R = alkyl

R' = alkyl, vinyl

as well as, for example, hexamethyldisilazane.

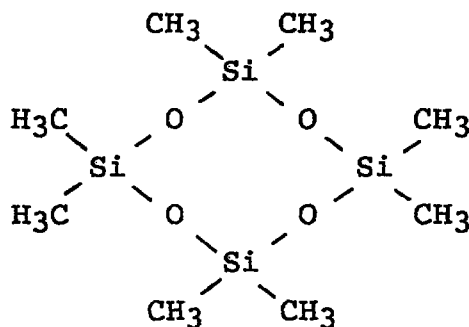
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The following substances in particular can be used as
siloxanes:

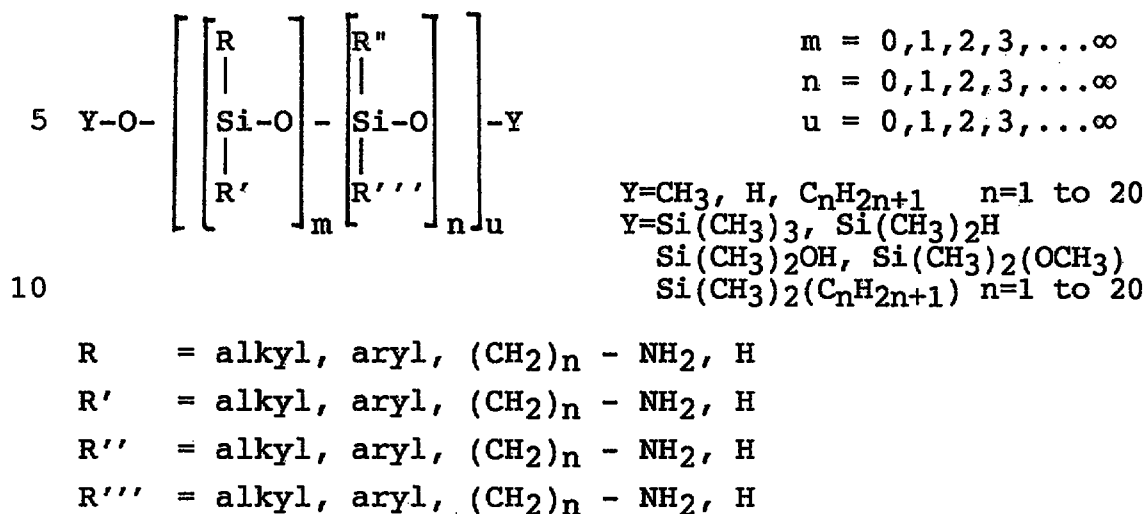
cyclic polysiloxanes of the type D 3, D 4, D 5

20 for example, octamethylcyclotetrasiloxane = D 4

25



Polysiloxanes or silicone oils of the type



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The invention also provides granules based on pyrogenically prepared silicon dioxide and having the following physicochemical properties:

20	Average grain size:	10 to 120 μm
	BET surface area:	40 to 400 m^2/g
	Pore volume:	0.5 to 2.5 ml/g
	Pore size distribution:	less than 5 % of the total pore volume exists of pores with a diameter < 5 nm, rest meso- and macropores
25	Carbon content:	0.3 to 15.0 wt. %
	pH value:	3.6 to 8.5
	Tapped density:	220 to 700 g/l

30

The granular material according to the invention preferably has meso- and macropores, with the volume of the mesopores constituting 10 to 80% of the total pore volume.

35 The carbon content of the granular material according to the invention may be from 0.3 to 15.0 wt. %.



The particle size distribution of the granular material according to the invention may be 80 vol.% larger than 8 μm and 80 vol.% smaller than 96 μm .

- 5 In a preferred embodiment of the invention, the proportion of pores smaller than 5 μm may be at most 5% referred to the total pore volume.

- The granular material according to the invention can be
10 prepared by dispersing pyrogenically prepared silicon dioxide in water, spray drying it, heating the granules obtained at a temperature of from 150 to 1,100°C for a period of 1 to 8 h and then silanising them. The same halosilanes, alkoxysilanes, silazanes and/or siloxanes
15 described above can be used for the silanisation.

- The invention further provides a method for the preparation of granules based on pyrogenically prepared silicon dioxide, which is characterised in that pyrogenically
20 prepared silicon dioxide, preferably silicon dioxide prepared from silicon tetrachloride by means of flame hydrolysis, is dispersed in water, spray dried, the granules obtained are optionally heated at a temperature of from 150 to 1,100°C for a period of 1 to 8 h and/or
25 silanised.

The dispersion in water can have a silicon dioxide concentration of from 5 to 25 wt.%.

- 30 The spray drying can be carried out at a temperature of from 200 to 600°C. Disc atomisers or nozzle atomisers can be used for this purpose.

- The heating of the granules can be carried out both in
35 fixed beds, for example chamber kilns, and in moving beds, for example rotary dryers.

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The silanisation can be carried out using the same halosilanes, alkoxysilanes, silazanes and/or siloxanes as described above, for which the silanising agent can be optionally dissolved in an organic solvent such as, for example, ethanol.

Preferably the silane Si 108 $[(CH_3O)_3Si-C_8H_{17}]$, trimethoxyoctylsilane, is used as silanising agent.

10 The silanisation can be carried out by spraying the granular material with the silanising agent and subsequently heat-treating the mixture at a temperature of from 105 to 400°C over a period of 1 to 6 h.

15 In an alternative method, the silanisation of the granules can be carried out by treating the granular material with the silanising agent in vapour form and subsequently heat-treating the mixture at a temperature of from 200 to 800°C over a period of 0.5 to 6 h.

20

The heat treatment can take place under protective gas such as, for example, nitrogen.

The silanisation can be carried out continuously or batchwise in heatable mixers and dryers equipped with spraying facilities. Examples of suitable devices are ploughshare mixers, disk dryers or fluidised bed dryers.

The physicochemical variables of the granules, such as the specific surface, the particle size distribution, the pore volume, the tamped density and the silanol group concentration, the pore distribution and pH value can be altered within the specified limits by varying the starting materials and the conditions during spraying, heating and silanisation.

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The granules according to the invention can be used as supports for polymerisation catalysts, in particular as supports for catalysts for the production of polyethylene.

- 5 They have the advantage of possessing a high purity, a high thermostability, a low silanol group concentration, primary particles microspherical in shape and less than 5 % of the total pore volume exists of pores with a diameter < 5 nm.

10

The invention further provides the use of the granules as catalyst supports, in particular for the production of polymerisation catalysts. In a preferred embodiment of the invention, the granules according to the invention can be

- 15 used as catalyst supports for producing catalysts for the production of polyethylene.

Examples

- 20 The pyrogenically prepared silicon dioxides used are silicon dioxides having the physicochemical properties given below.

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	AEROSIL 90	AEROSIL 130	AEROSIL 150	AEROSIL 200	AEROSIL 300	AEROSIL 380	AEROSIL OX50
CAS Reg. Number	112945-52-5 (former No.: 7631-86-9)						
Behaviour towards water	hydrophilic						
Appearance	loose white powder						
Surface area BET ¹⁾ m ² /g	90 ± 15	130 ± 25	150 ± 15	200 ± 25	300 ± 30	380 ± 30	50 ± 15
Average size of primary particles mm	20	16	14	12	7	7	40
Tamped density ²⁾ Normal ware g/l Compacted ware g/l (Addition "V")	ca. 80 -	ca. 50 ca. 120	ca. 50 ca. 120	ca. 50 ca. 120	ca. 50 ca. 120	ca. 50 ca. 120	ca. 130 -
Loss on drying ³⁾ (2 h at 105 °C) % on leaving the supplier	< 1.0	< 1.5	< 0.5 ⁹⁾	< 1.5	< 1.5	< 1.5	< 1.5
Loss on ignition ⁴⁾⁷⁾ (2 h at 1.000 °C) %	< 1	< 1	< 1	< 1	< 2	< 2,5	< 1
pH value ⁵⁾ (in 4% aqueous dispersion)	3.6 - 4.5	3.6 - 4.3	3.6 - 4.3	3.6 - 4.3	3.6 - 4.3	3.6 - 4.3	3.6 - 4.3
SiO ₂ ⁸⁾ %	> 99.8	> 99.8	> 99.8	> 99.8	> 99.8	> 99.8	> 99.8
Al ₂ O ₃ ⁸⁾ %	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.08
Fe ₂ O ₃ ⁸⁾ %	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.01
TiO ₂ ⁸⁾ %	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03
HCl ⁸⁾¹¹⁾ %	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025
Screen oversize ⁶⁾ (by Mocker, 45 µm) %	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	0.2

- 1) In accordance with DIN 66131
- 2) In accordance with DIN ISO 787/XI, JIS K 5101/18 (not screened)
- 3) In accordance with DIN ISO 787/II, ASTM D 280, JIS K 5101/21
- 4) In accordance with DIN 55921, ASTM D 1208, JIS K 5101/23
- 5) In accordance with DIN ISO 787/IX, ASTM D 1208, JIS K 5101/24
- 6) In accordance with DIN ISO 787/XVIII, JIS K 5101/20
- 7) Referred to the substance dried for 2 hours at 105°C
- 8) Referred to the substance calcined for 2 hours at 1000°C
- 9) Special moisture-resistant packaging
- 10) In water: ethanol 1 : 1
- 11) HCl content in constituent of the loss on ignition

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To prepare the silicon dioxides, a liquid silicon compound is sprayed into an oxyhydrogen flame consisting of hydrogen and air. In most cases silicon tetrachloride is used. This substance is hydrolysed to silicon dioxide and hydrochloric acid by the action of the water formed during the hydrogen-oxygen reaction. After leaving the flame, the silicon dioxide enters a so-called coagulation zone, wherein the primary Aerosil particles and primary Aerosil aggregates agglomerate. The product, which exists at this stage as a kind of aerosol, is separated from the accompanying gaseous substances in cyclones and then aftertreated with moist heated air.

By this process the residual hydrochloric acid content can be lowered to 0.025%. As the silicon dioxide obtained at the end of this process has a bulk density of only about 15 g/l, there is a subsequent vacuum compaction, whereby tamped densities of about 50 g/l and more can be established.

20

The particle sizes of the silicon dioxides can be varied by means of the reaction conditions such as, for example, flame temperature, proportions of hydrogen and oxygen, quantity of silicon tetrachloride, residence time in the flame or length of the coagulation path.

The BET surface area is determined using nitrogen in accordance with DIN 66 131.

30 The pore volume is calculated from the sum of the micro-, meso- and macropore volumes. The micro- and mesopores are determined by recording an N₂ isotherm and evaluation thereof by the methods of BET, de Boer and Barrett, Joyner and Halenda. The macropores $D > 30$ nm are determined by the Hg porosimetry method. For the determination of the macropores, the sample is dried for 15 h at 100°C in the drying oven and degassed at room temperature in a vacuum.



For the determination of the micro- and mesopores, the sample is dried for 15 h at 100°C in the drying oven and degassed for 1 h at 200°C in a vacuum.

- 5 The silanol group concentration is determined by the lithium alanate method. Here the SiOH- groups are reacted with LiAlH₄ and the quantity of hydrogen formed during this reaction is determined from the pressure.

10 Principle of measurement

The granular material is weighed into a four-necked flask. The flask is evacuated and an oil bath is heated to 150°C. The temperature in the flask (controlled by an internal
15 thermometer) rises with the temperature of the oil bath to about 130°C. The pressure during the preliminary treatment is recorded using a pressure measuring device PI₂ (TM 210, from Leybold, measuring range 10³ to 10⁻³ mbar). The
20 desorption of the water can be monitored from the pressure measurement. At the end of the preliminary treatment (30 min at the end temperature) a pressure of less than 10⁻² mbar must have been achieved.

After completion of the preliminary treatment, the
25 evacuated flask is separated from the vacuum unit by closing the stop valve and is brought to normal temperature. The actual measurement is based on a measured quantity of LiAlH₄ solution being introduced into the flask through the dropping funnel and the rise in pressure being
30 measured from the hydrogen formed. If the volume of the flask is known, the quantity of H₂ can be calculated from the ideal gas law. The pressure is recorded using a digital measuring device (PI₁) (MKS Instruments PR-2000), having a measuring range of between 0 and 1 bar.

35

The LiAlH₄ solution used (2% LiAlH₄ in diethylene glycol dimethyl ether) is degassed prior to the experiment being



carried out, in order to remove readily volatile constituents, which distort the pressure measurement. For this purpose the pressure above the solution in the dropping funnel is lowered by a second vacuum pump to the vapour pressure (3.7 mbar at 22°C), so that the liquid boils. A blank measurement without a sample is taken to test whether the solution is sufficiently degassed. In the determination of the hydrogen pressure, a correction is made using the vapour pressure of the solvent.

10

Interpretation

The apparatus is calibrated by first of all determining the volume of the dropping funnel provided with a ground-glass stopper, gauging the capacity in litres. The volume of the reaction flask inclusive of all connections as far as the stop valve is obtained by the following experiment:

The dropping funnel, filled with air at atmospheric pressure, is attached to the evacuated flask. A pressure compensation between the two volumes is then brought about by opening the tap of the dropping funnel. The pressure established is indicated by the digital measuring device. The volume of the reaction vessel is obtained from the mass balance. A volume V_R equal to 243.8 ml is obtained with the present arrangement.

The number of moles of hydrogen formed is obtained from the equations:

30

$$n = \frac{p \cdot V(\text{corr.})}{RT}$$

35

$$V_{\text{corr.}} = V_R - V_{\text{solids}} - V_{\text{solution}}$$



15

p is the increase in pressure in the reaction flask. This value is corrected by an amount corresponding to the vapour pressure of the solvent (3.7 mbar at 22°C). At room temperatures greatly differing from 22°C the vapour pressure is taken from the vapour pressure table. It is useful so to select the weighed sample, that a value for p of between 200 and 800 mbar is obtained. In this case minor changes in the vapour pressure owing to temperature variations have hardly any effect on the result.

10

The volume of the reaction vessel is corrected by deducting the volume of solid matter and the volume of the solution introduced. The former is given from the weighed portion and the density and the latter is read from the dropping funnel.

15

The density of silanol groups is finally obtained from the equation:

20

$$d = \frac{n \cdot N_L}{F}$$

N_L : Lohschmidt number

25 F: Surface of the weighed solid matter

The samples are treated as follows:

1 h heating at 120°C and 0.2 mbar; cooling to 60°C;
30 addition of LiAlH_4 ; after 10 mins, reading the pressure difference which has arisen.

The particle size distribution is determined by means of the laser optical particle size analyser Cilas Granulametre
35 715.

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The tapped volume is determined in accordance with ASTM D 4164-88.

Equipment: Tapping volumeter STA V 2003 from
Engelsmann, in accordance with DIN 53194,
section 5.2. b-f
Measuring cylinder 250 ml, graduation marks
every 2 ml
Balance with limit of error of max. ± 0.1 g

Procedure

The counter of the tapping volumometer is set to 1000 strokes.

15 The measuring cylinder is tared.

The granular material is placed in the measuring cylinder up to the 250 ml mark.

The weight of the sample is recorded (± 0.1 g).

20 The measuring cylinder is placed in the volumeter and the apparatus is switched on.

End of tapping: the apparatus automatically switches off after 1000 strokes

The tapped bulk volumes are read to an accuracy of 1 ml.

25 Calculation

E: weighed portion of granular material in g

V: volume read in ml

30 W: water content in wt.% (determined in accordance with Specification P001)

$$\text{Tapped density} = \frac{E \times (100 - W)}{V \times 100}$$

35

The pH value is determined in 4% aqueous dispersion, in the case of hydrophobic catalyst supports in water:ethanol 1:1.



Preparation of the granules according to the invention

- The pyrogenically prepared silicon dioxide is dispersed in completely demineralised water. A dispersing aggregate
5 which operates according to the rotor/stator principle is used in the process. The suspensions formed are spray dried. The finished product is precipitated by a filter or cyclone.
- 10 The sprayed granules are heated in a muffle furnace.
- The spray-dried and optionally heated granules are placed in a mixer for the silanisation process and sprayed with intensive mixing optionally first of all with water and
15 then with the silane Si 108 (trimethoxyoctylsilane) or HMDS (hexamethyldisilazane). After spraying has been completed, the material is mixed for 15 to 30 more minutes and then heated for 1 to 4 h at 100 to 400°C.
- 20 The water used can be acidified with an acid, for example, hydrochloric acid, to a pH value of 7 to 1. The silanising agent used can be dissolved in a solvent such as, for example, ethanol.

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<i>Example</i>	<i>Comparison 1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>Comparison 5</i>
Starting Aerosil	380	380	380	380	380
Data for spray drying					
Quantity of H ₂ O (kg)	10	10	105	105	15
Quantity of Aerosil (kg)	1.5	1.5	14.7	14.7	1.5
Atomisation using	Disc	Disc	Disc	Disc	Disc
Operating temperature (°C)	380	380	380	440	380
Exhaust air temperature (°C)	105	105	105	108	105
Precipitation	Filter	Filter	Filter	Filter	Cyclone
Data for heating (h/°C)	-	-	2/700	2/700	-
Data for the modification of the surface					
Reagent	-	Si 108	Si 108	HMDS	-
Quantity [g/100 g Aerosil]	-	25	25	20	-
Quantity of water [g/100 g Aerosil]	-	-	5	5	-
Heating time (h)	-	2	2	4	-
Temperature (°C)	-	120	120	140	-
Physicochemical properties					
BET surface area (m ² /g)	350	197	189	212	277
Pore volume (ml/g)	2.09	1.69	1.55	1.68	1.69
Pore volume (% of total pore volume) in pores < 5 nm	n.d.	1.8	n.d.	n.d.	n.d.
Mesopores 2-30 nm (ml/g)	1.34	1.04	1.12	1.17	0.66
Makropores > 30 nm (ml/g)	0.75	0.65	0.43	0.51	1.03
Particle size d ₅₀ (µm)	38	40	66	53	39
Tapped volume (g/l)	320	390	420	370	260
pH value	4.7	5.0	5.6	7.2	4.8
Carbon content %	-	10.9	10.4	3.8	-
Silanol group concentration (mmol OH/g)	1.80	1.18	0.74	0.37	1.50

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<i>Example</i>	6	7	8	Compara- son 9	10
Starting Aerosil	300	300	300	0 x 50	0 x 50
Data for spray drying					
Quantity of H ₂ O (kg)	15	105	105	10	10
Quantity of Aerosil (kg)	1.5	14.7	14.7	1.5	1.5
Atomisation using	Disc	Single nozzle	Double nozzle	Disc	Disc
Operating temperature (°C)	380	440	440	380	380
Exhaust air temperature (°C)	105	108	108	105	105
Precipitation	Cyclone	Filter	Filter	Cyclone	Cyclone
Data for heating (h/°C)			2/700		
Data for the modification of the surface					
Reagent	HMDS	Si 108	HMDS	-	HMDS
Quantity [g/100 g Aerosil]	15	25	20	-	3
Quantity of water [g/100 g Aerosil]	5	5	5	-	-
Heating time (h)	4	2	4	-	5
Temperature (°C)	140	120	140	-	140
Physicochemical properties					
BET surface area (m ² /g)	222	180	195	46	41
Pore volume (ml/g)	1.79	1.49	1.51	0.73	0.68
Pore volume (% of total pore volume) in pores < 5 nm	n.d.	1.7	1.5	n.d.	1.2
Mesopores 2-30 nm (ml/g)	0.78	0.60	0.60	0.08	0.09
Makropores > 30 nm (ml/g)	1.01	0.89	0.91	0.65	0.59
Particle size d ⁵⁰ (µm)	32	40	43	21	21
Tapped volume (g/l)	290	320	300	540	570
pH value	6	5.2	6.9	5.3	7.4
Carbon content %	2.7	9.3	3.3	-	0.5
Silanol group concentration (mmol OH/g)	0.61	1.15	0.40	0.29	0.14



<i>Example</i>	<i>Compara- son 11</i>	<i>12</i>	<i>Compara- son 13</i>	<i>14</i>
Starting Aerosil	130	130	200	200
Data for spray drying				
Quantity of H ₂ O (kg)	15	115	15	15
Quantity of Aerosil (kg)	1.5	1.5	1.5	1.5
Atomisation using	Disc	Disc	Disc	Disc
Operating temperature (°C)	380	380	380	380
Exhaust air temperature (°C)	105	105	105	105
Precipitation	Cyclone	Cyclone	Cyclone	Cyclone
Data for heating (h/°C)	-	-	-	-
Data for the modification of the surface				
Reagent	-	HMDS	-	HMDS
Quantity [g/100 g Aerosil]	-	5	-	7
Quantity of water [g/100 g Aerosil]	-	-	-	-
Heating time (h)	-	5	-	5
Temperature (°C)	-	140	-	140
Physicochemical properties				
BET surface area (m ² /g)	131	111	196	153
Pore volume (ml/g)	1.92	1.62	2.25	2.04
Pore volume (% of total pore volume) in pores < 5 nm	n.d.	1.7	n.d.	0.9
Mesopores 2-30 nm (ml/g)	0.24	0.24	0.46	0.47
Makropores > 30 nm (ml/g)	1.68	1.38	1.79	1.57
Particle size d ₅₀ (µm)	20	20	14	14
Tapped volume (g/l)	250	280	230	240
pH value	4.8	7.3	4.8	7.2
Carbon content %	-	1.3	-	1.7
Silanol group concentration (mmol OH/g)	0.83	0.44	1.16	0.56



The particle size distributions of the granules obtained according to Examples 1 to 14 are represented in tabular and graphical form in Figures 1 to 4.

- 5 Examples 1, 5, 9, 11 and 13 are comparative Examples from prior art (DE-A 36 11 449 Liu).

10 Examples of the use of the granules according to the invention as catalyst supports in the production of polyethylene

Referred to the active component titanium, the catalysts achieved the following results in the polymerisation of ethylene:

15

Catalyst on a support Example	Yield kg PE/g Ti	Comment
Example 1	292	Only spray-dried support as in Example 1
Example 2	360	Chemically treated support as in Example 4
Example 3	376	Heat-treated and chemically treated support as in Example 6



22



Claims

1. Granules based on pyrogenically prepared silicon dioxide and having the following physicochemical properties:
- 5
- Average grain size: 10 to 120 μm
BET surface area: 40 to 400 m^2/g
Pore volume: 0.5 to 2.5 ml/g
10 Pore size distribution: less than 5 % of the total pore volume exists of pores with a diameter < 5 nm, rest meso- and macropores
pH value: 3.6 to 8.5
15 Tapped density: 220 to 700 g/l
2. Method for the preparation of the granules according to claim 1, characterised in that pyrogenically prepared silicon dioxide is dispersed in water and spray dried and the granules obtained are heated at a temperature of from 150 to 1,100°C for a period of 1 to 8 h.
- 20
3. Granules based on pyrogenically prepared silicon dioxide and having the following physicochemical properties:
- 25
- Average grain size: 10 to 120 μm
BET surface area: 40 to 400 m^2/g
30 Pore volume: 0.5 to 2.5 ml/g
Pore size distribution: less than 5 % of the total pore volume exists of pores with a diameter < 5 nm, rest meso- and macropores
pH value: 3.6 to 8.5
35 Tapped density: 220 to 700 g/l



4. Method for the preparation of the granules according to claim 3, characterised in that pyrogenically prepared silicon dioxide is dispersed in water and spray dried and the granules obtained are silanised.
- 5
5. Granules based on pyrogenically prepared silicon dioxide and having the following physicochemical properties:
- | | | |
|----|-------------------------|--|
| 10 | Average grain size: | 10 to 120 μm |
| | BET surface area: | 40 to 400 m^2/g |
| | Pore volume: | 0.5 to 2.5 ml/g |
| | Pore size distribution: | less than 5 % of the total pore volume exists of pores with a diameter < 5 nm, rest meso- and macropores |
| 15 | pH value: | 3.6 to 8.5 |
| | Tapped density: | 220 to 700 g/l |
- 20 6. Method for the preparation of the granules according to claim 5, characterised in that pyrogenically prepared silicon dioxide is dispersed in water and spray dried and the granules obtained are heated at a temperature of from 150 to 1,100°C for a period of 1
- 25 to 8 h and subsequently silanised.
7. Method for the preparation of granules based on pyrogenically prepared silicon dioxide according to claims 1, 3 and 5, characterised in that pyrogenically prepared silicon dioxide, preferably silicon dioxide prepared from silicon tetrachloride by means of flame hydrolysis, is dispersed in water, spray dried, the granules obtained are optionally heated at a
- 30 temperature of from 150 to 1,100°C for a period of 1
- 35 to 8 h and/or silanised.

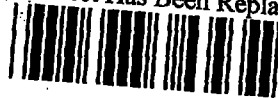
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8. Use of the granules according to claims 1, 3 and 5 as catalyst supports, in particular for the production of polymerisation catalysts.
- 5 9. Use of the granules according to claims 1, 3 and 5 as catalyst supports for producing catalysts for the production of polyethylene.



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Granules based on pyrogenically prepared
silicon dioxide, method for their preparation and
use thereof

5

Abstract

Granules based on silicon dioxide and having the
10 properties:

Average grain size: 10 to 120 μm

BET surface area: 40 to 400 m^2/g

Pore volume: 0.5 to 2.5 ml/g

15 Pore size distribution: less than 5 % of the total pore
volume exists of pores with a
diameter < 5 nm, rest meso- and
macropores

pH value: 3.6 to 8.5

20 Tapped density: 220 to 700 g/l

They are prepared by dispersing silicon dioxide in water,
spray drying, optionally heating and/or silanising.

25 The granules are used as catalyst supports.

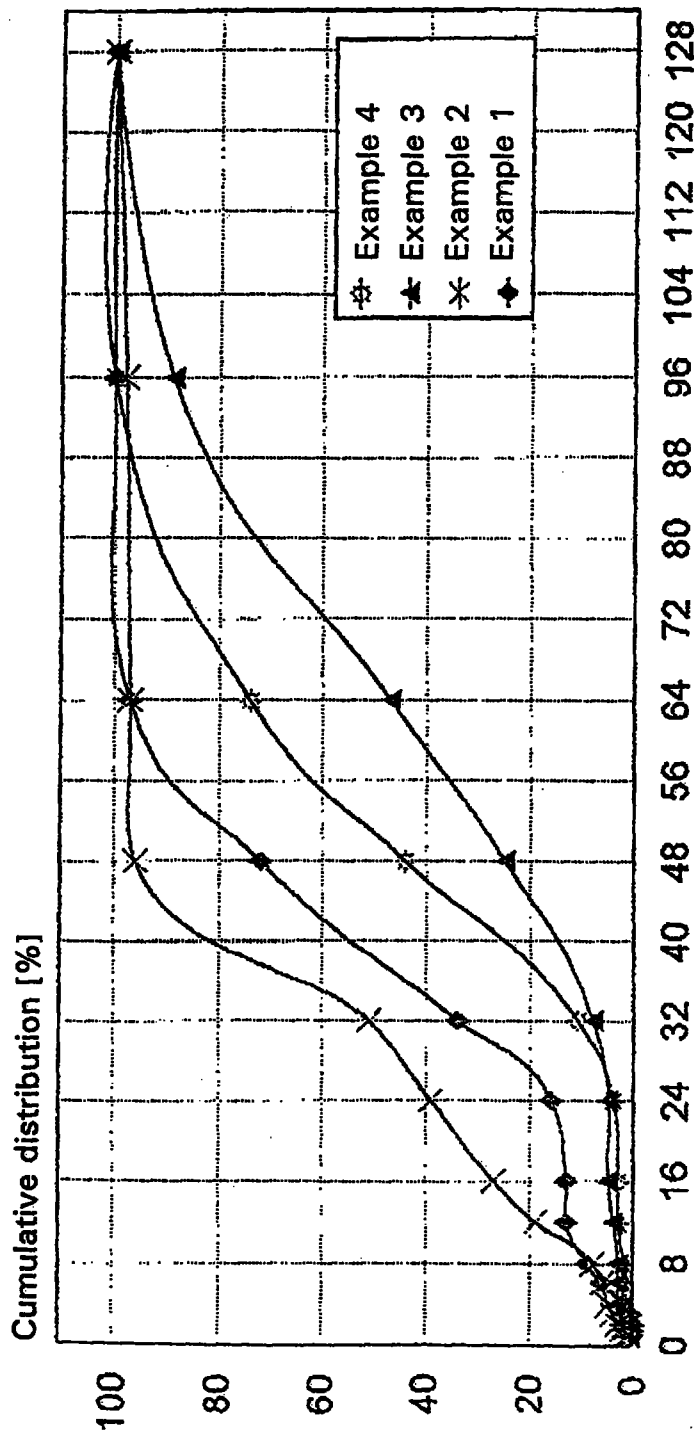
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Particle size distribution Si oxide support



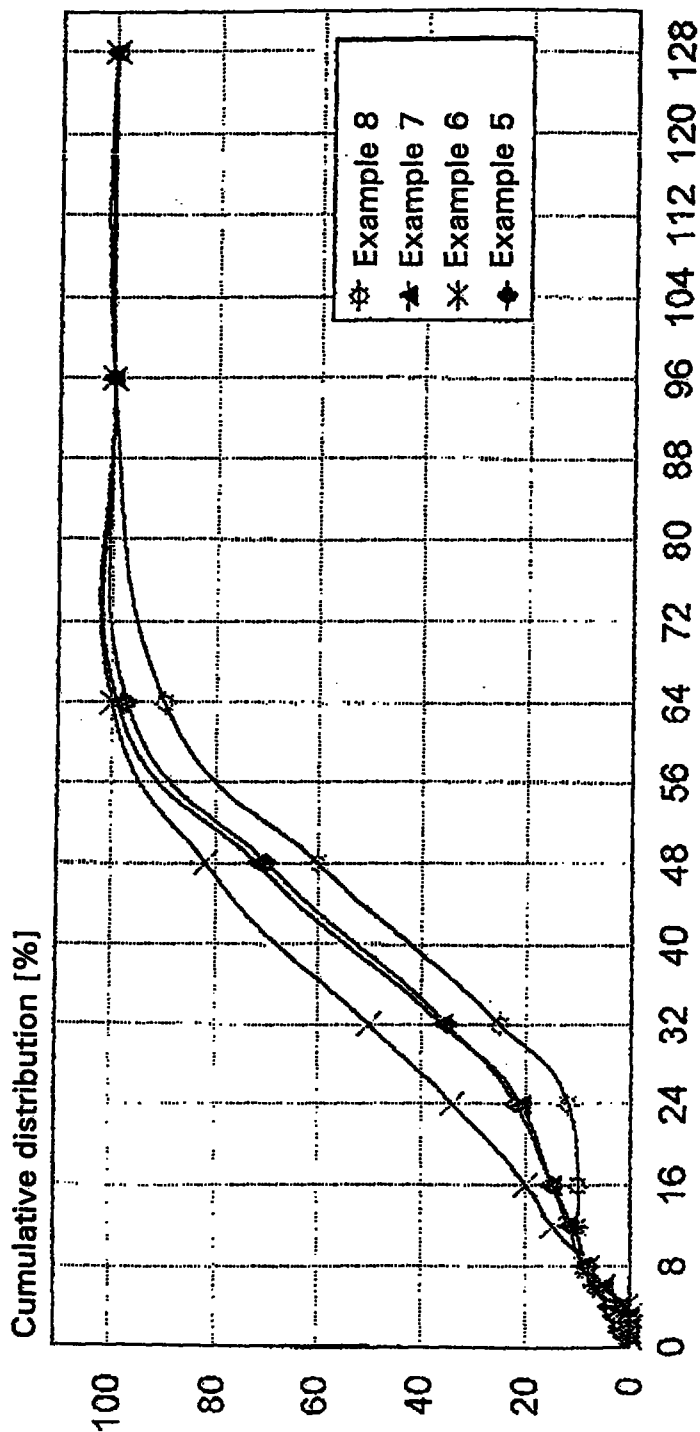
		particle size																[μm]			
		1	1,5	2	3	4	6	8	12	16	24	32	48	64	96	128					
Example 1	0	0	0	0	0,4	2	6	9	13	13	16	34	72	97	100	100	[%]				
Example 2	1	2	3	4	5	6	6	8	19	27	39	51	96	97	98	100	[%]				
Example 3	0,4	0,6	0,8	2	3	3	3	3	4	5	5	8	25	47	89	100	[%]				
Example 4	2	2	2	2	2	2	2	2	3	3	4	11	44	74	100	100	[%]				

Figure 1

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Particle size distribution Si oxide support



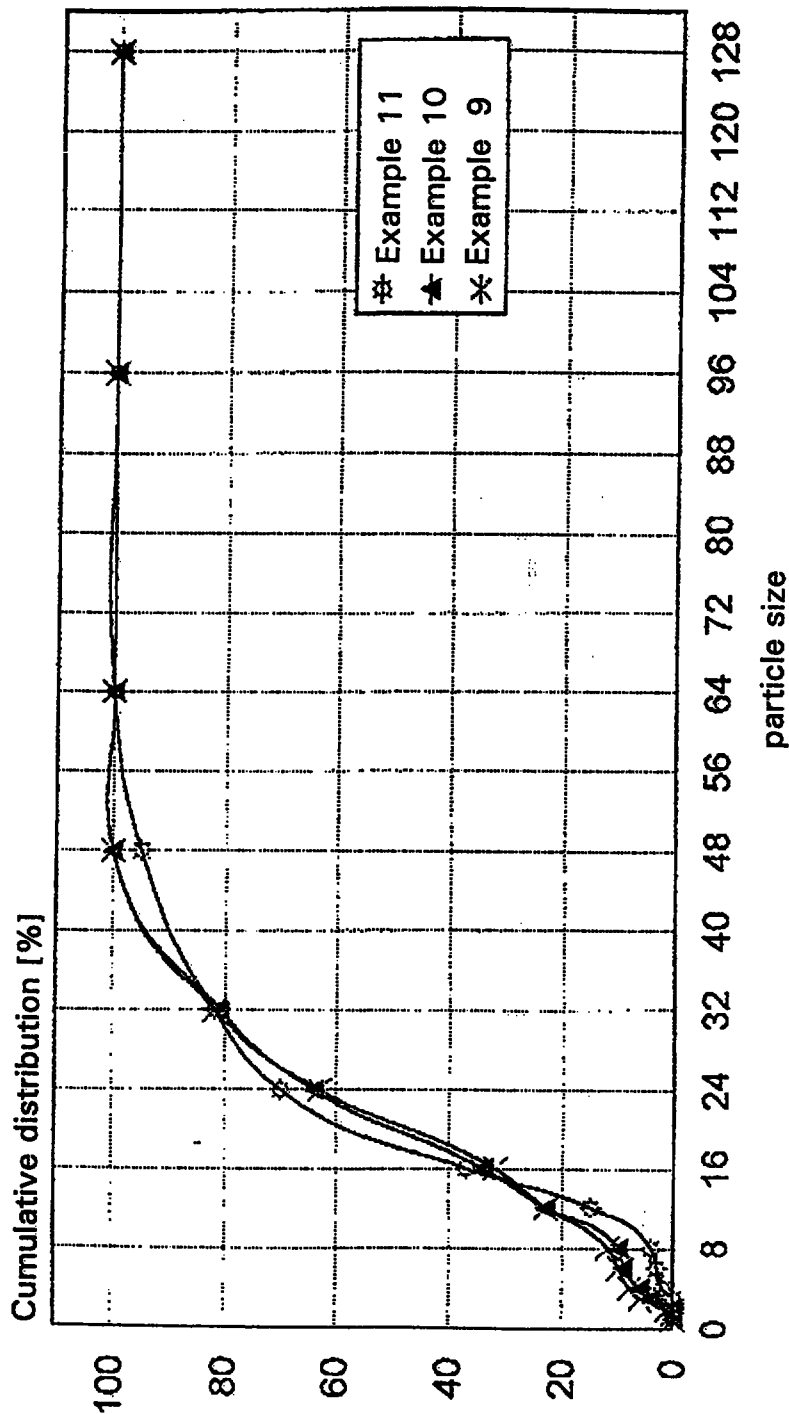
		particle size																			
		1	1,5	2	3	4	6	8	12	16	24	32	48	64	96	128	[μ m]				
Example 5	1	1	2	2	3	4	6	8	11	15	22	35	70	97	100	100	100	[%]			
Example 6	0	0	0	0	0	0,9	5	8	15	20	34	50	82	100	100	100	100	[%]			
Example 7	0	0	0	0	0	2	5	9	12	15	21	36	72	99	100	100	100	[%]			
Example 8	0,1	0,1	0,2	1	4	4	7	9	10	10	12	25	60	90	100	100	100	[%]			

Figure 2

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Particle size distribution Si oxide support



	1	1,5	2	3	4	6	8	12	16	24	32	48	64	96	128	[μm]
Example 9	0,1	0,1	1	6	8	10	12	23	32	63	82	100	100	100	100	100
Example 10	0	0	0,1	4	6	9	10	23	34	64	81	100	100	100	100	100
Example 11	0	0	0	0	2	3	4	15	37	70	82	95	100	100	100	100
																[%]

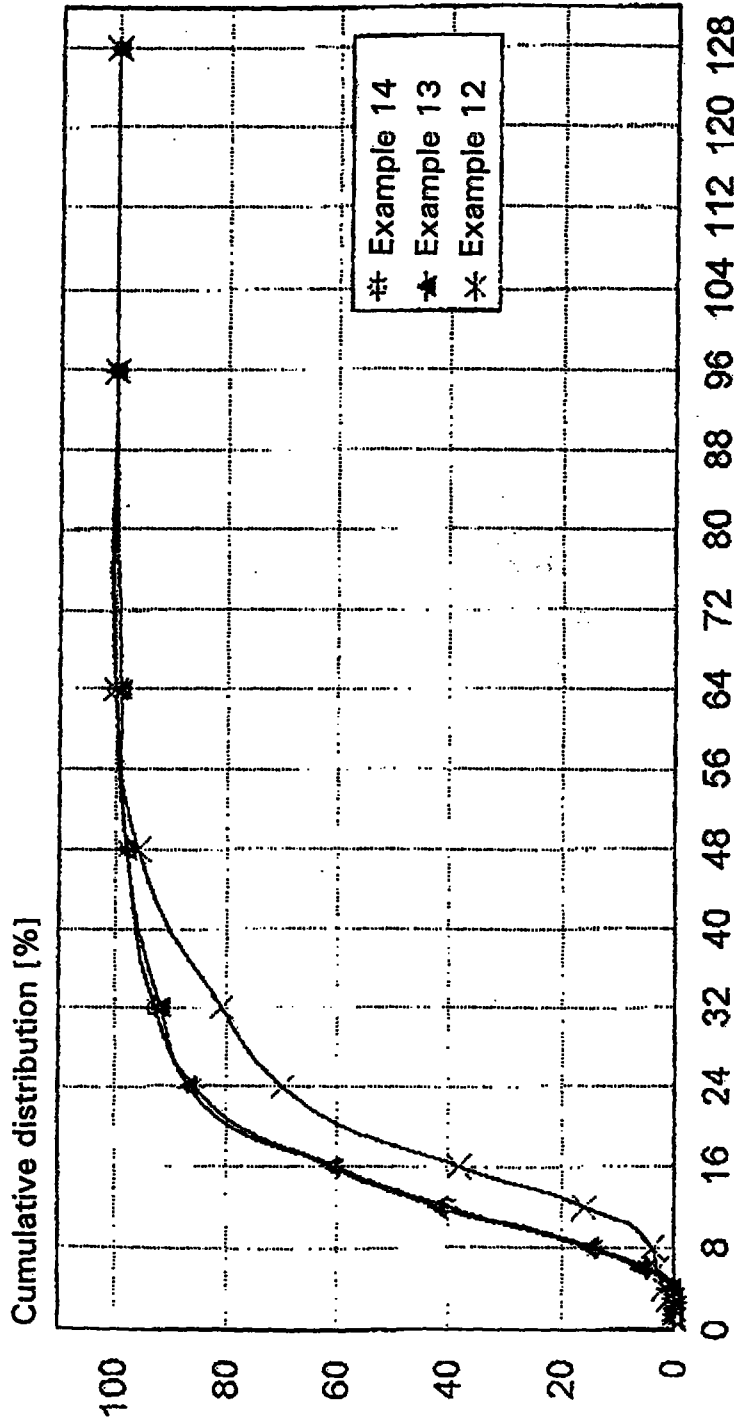
Figure 3

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Particle size distribution Si oxide support



		particle size																			
		1	1,5	2	3	4	6	8	12	16	24	32	48	64	96	128	[μ m]				
Example 12	0	0	0	0	1	2	3	4	16	38	70	81	96	100	100	100	100	[%]			
Example 13	0	0	0	0	0	0,5	6	15	42	61	87	92	98	99	100	100	100	[%]			
Example 14	0	0	0	0	0	0	5	14	40	60	86	93	98	100	100	100	100	[%]			

Figure 4

Granules based on pyrogenically prepared
silicon dioxide, method for their preparation and
use thereof

- 5 The invention relates to granules based on pyrogenically prepared silicon dioxide, the method for their preparation and the use thereof as catalyst supports.

The preparation of pyrogenic silicas or silicon dioxides
10 from SiCl_4 by means of high-temperature-or flame hydrolysis is known (Ullmanns Enzyklopädie der technischen Chemie, 4th Edition, Volume 21, page 464 (1982)).

Pyrogenic silicon dioxides are distinguished by having
15 extremely fine particles, high specific surface (BET), very high purity, spherical particle shape and the absence of pores. On account of these properties pyrogenically prepared silicon dioxides are attracting increasing interest as supports for catalysts (Dr. Koth et al., Chem.
20 Ing. Techn. 52, 628 (1980)). For this application the pyrogenically prepared silicon dioxide is shaped by mechanical means, for example, tableting machines.

The shaping of pyrogenically prepared silicon dioxide into
25 sprayed granules also by means of spray drying, to obtain a starting material for sintered ceramic materials, is also known (DE-A 36 11 449).

It is also known that silicon dioxide pyrogenically
30 prepared in an electric arc may be shaped by means of spray drying into sprayed granules, which can be used as adsorption media or else as catalyst supports (DE-A 12 09 108).

35 The subjection of pyrogenically prepared silicon dioxide to a gel process and the subsequent shaping into granules by means of spray drying is also known. These granules, after

coating with chromium oxide, are used in the polymerisation of ethylene (EP-A 0 050 902, US-A 4,386,016).

Furthermore, the use of precipitated silicon dioxide as a catalyst support for the catalytic polymerisation of olefins is known (WO 91/09881).

The known sprayed granules of pyrogenically prepared silicon dioxides have the disadvantage that they are not optimally suitable for use as catalyst supports, for example, in the production of polyethylene.

The object was therefore the development from pyrogenically prepared silicon dioxide of sprayed granules which can be used as catalyst supports in the production of polyethylene.

The present invention provides granules based on pyrogenically prepared silicon dioxide and having the following physicochemical properties:

Average grain size:	10 to 120 μm
BET surface area:	40 to 400 m^2/g
Pore volume:	0.5 to 2.5 ml/g
Pore size distribution:	less than 5 % of the total pore volume exists of pores with a diameter < 5 nm, rest meso- and macropores
pH value:	3.6 to 8.5
Tapped density:	220 to 700 g/l

The granular material according to the invention can be prepared by dispersing pyrogenically prepared silicon dioxide in water, spray drying it and heating the granules obtained at a temperature of from 150 to 1,100°C for a period of 1 to 8 h.

The invention also provides granules based on pyrogenically prepared silicon dioxide and having the following physicochemical properties:

- 5 Average grain size: 10 to 120 μm
 BET surface area: 40 to 400 m^2/g
 Pore volume: 0.5 to 2.5 ml/g
 Pore size distribution: less than 5 % of the total pore
 10 volume exists of pores with a
 diameter < 5 nm, rest meso- and
 macropores
 pH value: 3.6 to 8.5
 Tapped density: 220 to 700 g/l

- 15 The granular material according to the invention can be
 prepared by dispersing pyrogenically prepared silicon
 dioxide in water, spray drying it and silanising the
 granules obtained. Halosilanes, alkoxysilanes, silazanes
 and/or siloxanes can be used for the silanisation.

- 20 The following substances in particular can be used as
 halosilanes:

- 25 Haloorganosilanes of the type $\text{X}_3 \text{Si}(\text{C}_n\text{H}_{2n+1})$ X = Cl, Br
 n = 1 to 20

Haloorganosilanes of the type $\text{X}_2 (\text{R}')\text{Si}(\text{C}_n\text{H}_{2n+1})$ X = Cl, Br
 R' = alkyl
 n = 1 to 20

- 30 Haloorganosilanes of the type $\text{X}(\text{R}')_2 \text{Si}(\text{C}_n\text{H}_{2n+1})$ X = Cl, Br
 R' = alkyl
 n = 1 to 20

Haloorganosilanes of the type $X_3 Si(CH_2)_m-R'$

$X = Cl, Br$

$m = 0.1 \text{ to } 20$

$R' = \text{alkyl, aryl (for example, } -C_6H_5)$

- 5 $-C_4F_9, -OCF_2-CHF-CF_3, -C_6F_{13}, -O-CF_2-CHF_2$
 $-NH_2, -N_3, -SCN, -CH=CH_2,$
 $-OOC(CH_3)C = CH_2$
 $-OCH_2-CH(O)CH_2$
 $-NH-CO-\underline{N-CO-(CH_2)_5}$
 10 $-NH-COO-CH_3, -NH-COO-CH_2-CH_3, -NH-(CH_2)_3Si(OR)_3$
 $-S_x-(CH_2)_3Si(OR)_3$

Haloorganosilanes of the type $(R)_X Si(CH_2)_m-R'$

$X = Cl, Br$

15 $R = \text{alkyl}$

$m = 0.1 \text{ to } 20$

$R' = \text{alkyl, aryl (for example, } -C_6H_5)$

- $-C_4F_9, -OCF_2-CHF-CF_3, -C_6F_{13}, -O-CF_2-CHF_2$
 $-NH_2, -N_3, -SCN, -CH=CH_2,$
 20 $-OOC(CH_3)C = CH_2$
 $-OCH_2-CH(O)CH_2$
 $-NH-CO-\underline{N-CO-(CH_2)_5}$
 $-NH-COO-CH_3, -NH-COO-CH_2-CH_3, -NH-(CH_2)_3Si(OR)_3$
 $-S_x-(CH_2)_3Si(OR)_3$

25

Haloorganosilanes of the type $(R)_2 X Si(CH_2)_m-R'$

$X = Cl, Br$

$R = \text{alkyl}$

$m = 0.1 \text{ to } 20$

30 $R' = \text{alkyl, aryl (for example, } -C_6H_5)$

- $-C_4F_9, -OCF_2-CHF-CF_3, -C_6F_{13}, -O-CF_2-CHF_2$
 $-NH_2, -N_3, -SCN, -CH=CH_2,$
 $-OOC(CH_3)C = CH_2$
 $-OCH_2-CH(O)CH_2$
 35 $-NH-CO-\underline{N-CO-(CH_2)_5}$
 $-NH-COO-CH_3, -NH-COO-CH_2-CH_3, -NH-(CH_2)_3Si(OR)_3$
 $-S_x-(CH_2)_3Si(OR)_3$

The following substances in particular can be used as alkoxysilanes:

- 5 Organosilanes of the type $(RO)_3 Si(C_nH_{2n+1})$ $R = \text{alkyl}$
 $n = 1 \text{ to } 20$

Organosilanes of the type $R'_x (RO)_y Si(C_nH_{2n+1})$ $R = \text{alkyl}$
 $R' = \text{alkyl}$
 $n = 1 \text{ to } 20$

- 10 $x+y = 3$
 $x = 1, 2$
 $y = 1, 2$

Organosilanes of the type $(RO)_3 Si(CH_2)_m-R'$

- 15 $R = \text{alkyl}$
 $m = 0.1 \text{ to } 20$
 $R' = \text{alkyl, aryl (for example, } -C_6H_5)$
 $-C_4F_9, -OCF_2-CHF-CF_3, -C_6F_{13}, -O-CF_2-CHF_2$
 $-NH_2, -N_3, -SCN, -CH=CH_2,$
20 $-OOC(CH_3)C = CH_2$
 $-OCH_2-CH(O)CH_2$
 $-NH-CO-N-CO-(CH_2)_5$
 $-NH-COO-CH_3, -NH-COO-CH_2-CH_3, -NH-(CH_2)_3Si(OR)_3$
 $-S_x-(CH_2)_3Si(OR)_3$

- 25 Organosilanes of the type $(R'')_x (RO)_y Si(CH_2)_m-R'$

$R'' = \text{alkyl}$ $x+y = 2$
 $x = 1, 2$
 $y = 1, 2$

- 30 $R' = \text{alkyl, aryl (for example, } -C_6H_5)$
 $-C_4F_9, -OCF_2-CHF-CF_3, -C_6F_{13}, -O-CF_2-CHF_2$
 $-NH_2, -N_3, -SCN, -CH=CH_2,$
 $-OOC(CH_3)C = CH_2$
 $-OCH_2-CH(O)CH_2$
35 $-NH-CO-N-CO-(CH_2)_5$
 $-NH-COO-CH_3, -NH-COO-CH_2-CH_3, -NH-(CH_2)_3Si(OR)_3$
 $-S_x-(CH_2)_3Si(OR)_3$

Preferably the silane Si 108 $[(CH_3O)_3Si-C_8H_{17}]$, trimethoxyoctylsilane, is used as silanising agent.

The following substances in particular can be used as
5 silazanes:

silazanes of the type $R'R_2Si-N-SiR_2R'$



10

R = alkyl

R' = alkyl, vinyl

as well as, for example, hexamethyldisilazane.

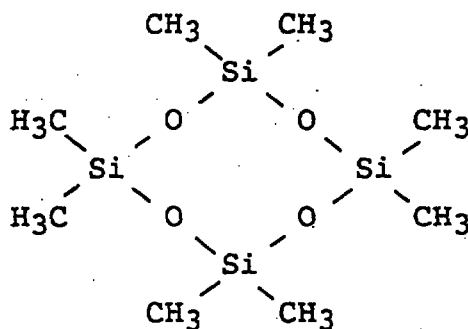
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The following substances in particular can be used as
siloxanes:

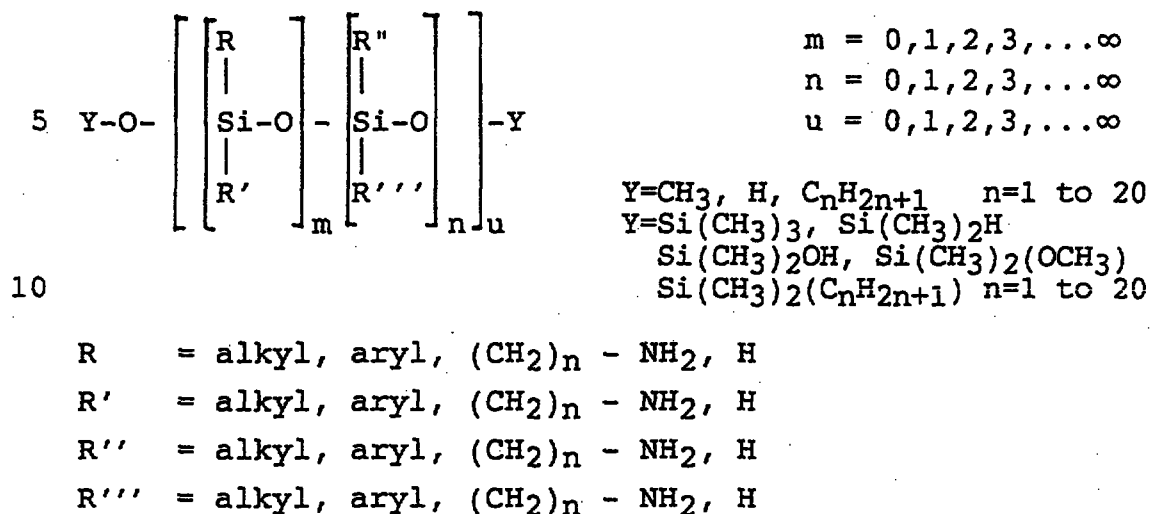
cyclic polysiloxanes of the type D 3, D 4, D 5

20 for example, octamethylcyclotetrasiloxane = D 4

25



Polysiloxanes or silicone oils of the type



15

The invention also provides granules based on pyrogenically prepared silicon dioxide and having the following physicochemical properties:

- 20 Average grain size: 10 to 120 μm
 BET surface area: 40 to 400 m^2/g
 Pore volume: 0.5 to 2.5 ml/g
 Pore size distribution: less than 5 % of the total pore volume exists of pores with a diameter < 5 nm, rest meso- and macropores
- 25 Carbon content: 0.3 to 15.0 wt. %
 pH value: 3.6 to 8.5
 Tapped density: 220 to 700 g/l

30

The granular material according to the invention preferably has meso- and macropores, with the volume of the mesopores constituting 10 to 80% of the total pore volume.

- 35 The carbon content of the granular material according to the invention may be from 0.3 to 15.0 wt. %.

The particle size distribution of the granular material according to the invention may be 80 vol.% larger than 8 μm and 80 vol.% smaller than 96 μm .

- 5 In a preferred embodiment of the invention, the proportion of pores smaller than 5 μm may be at most 5% referred to the total pore volume.

The granular material according to the invention can be
10 prepared by dispersing pyrogenically prepared silicon dioxide in water, spray drying it, heating the granules obtained at a temperature of from 150 to 1,100°C for a period of 1 to 8 h and then silanising them. The same halosilanes, alkoxysilanes, silazanes and/or siloxanes
15 described above can be used for the silanisation.

The invention further provides a method for the preparation of granules based on pyrogenically prepared silicon dioxide, which is characterised in that pyrogenically
20 prepared silicon dioxide, preferably silicon dioxide prepared from silicon tetrachloride by means of flame hydrolysis, is dispersed in water, spray dried, the granules obtained are optionally heated at a temperature of from 150 to 1,100°C for a period of 1 to 8 h and/or
25 silanised.

The dispersion in water can have a silicon dioxide concentration of from 5 to 25 wt.%.

- 30 The spray drying can be carried out at a temperature of from 200 to 600°C. Disc atomisers or nozzle atomisers can be used for this purpose.

The heating of the granules can be carried out both in
35 fixed beds, for example chamber kilns, and in moving beds, for example rotary dryers.

The silanisation can be carried out using the same halosilanes, alkoxysilanes, silazanes and/or siloxanes as described above, for which the silanising agent can be optionally dissolved in an organic solvent such as, for example, ethanol.

Preferably the silane Si 108 $[(CH_3O)_3Si-C_8H_{17}]$, trimethoxyoctylsilane, is used as silanising agent.

- 10 The silanisation can be carried out by spraying the granular material with the silanising agent and subsequently heat-treating the mixture at a temperature of from 105 to 400°C over a period of 1 to 6 h.
- 15 In an alternative method, the silanisation of the granules can be carried out by treating the granular material with the silanising agent in vapour form and subsequently heat-treating the mixture at a temperature of from 200 to 800°C over a period of 0.5 to 6 h.
- 20 The heat treatment can take place under protective gas such as, for example, nitrogen.

The silanisation can be carried out continuously or batchwise in heatable mixers and dryers equipped with spraying facilities. Examples of suitable devices are ploughshare mixers, disk dryers or fluidised bed dryers.

The physicochemical variables of the granules, such as the specific surface, the particle size distribution, the pore volume, the tamped density and the silanol group concentration, the pore distribution and pH value can be altered within the specified limits by varying the starting materials and the conditions during spraying, heating and silanisation.

The granules according to the invention can be used as supports for polymerisation catalysts, in particular as supports for catalysts for the production of polyethylene.

- 5 They have the advantage of possessing a high purity, a high thermostability, a low silanol group concentration, primary particles microspherical in shape and less than 5 % of the total pore volume exists of pores with a diameter < 5 nm.

10

- The invention further provides the use of the granules as catalyst supports, in particular for the production of polymerisation catalysts. In a preferred embodiment of the invention, the granules according to the invention can be
15 used as catalyst supports for producing catalysts for the production of polyethylene.

Examples

- 20 The pyrogenically prepared silicon dioxides used are silicon dioxides having the physicochemical properties given below.

	AEROSIL 90	AEROSIL 130	AEROSIL 150	AEROSIL 200	AEROSIL 300	AEROSIL 380	AEROSIL OX50
CAS Reg. Number	112945-52-5 (former No.: 7631-86-9)						
Behaviour towards water	hydrophilic						
Appearance	loose white powder						
Surface area BET ¹⁾ m ² /g	90 ± 15	130 ± 25	150 ± 15	200 ± 25	300 ± 30	380 ± 30	50 ± 15
Average size of primary particles mm	20	16	14	12	7	7	40
Tamped density ²⁾ Normal ware g/l Compacted ware g/l (Addition "V")	ca. 80 -	ca. 50 ca. 120	ca. 50 ca. 120	ca. 50 ca. 120	ca. 50 ca. 120	ca. 50 ca. 120	ca. 130 -
Loss on drying ³⁾ (2 h at 105 °C) % on leaving the supplier	< 1.0	< 1.5	< 0.5 ⁹⁾	< 1.5	< 1.5	< 1.5	< 1.5
Loss on ignition ⁴⁾⁷⁾ (2 h at 1.000 °C) %	< 1	< 1	< 1	< 1	< 2	< 2,5	< 1
pH value ⁵⁾ (in 4% aqueous dispersion)	3.6 - 4.5	3.6 - 4.3	3.6 - 4.3	3.6 - 4.3	3.6 - 4.3	3.6 - 4.3	3.6 - 4.3
SiO ₂ ⁸⁾ %	> 99.8	> 99.8	> 99.8	> 99.8	> 99.8	> 99.8	> 99.8
Al ₂ O ₃ ⁸⁾ %	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.08
Fe ₂ O ₃ ⁸⁾ %	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.01
TiO ₂ ⁸⁾ %	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03
HCl ⁸⁾¹¹⁾ %	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025
Screen oversize ⁶⁾ (by Mocker, 45 µm) %	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	0.2

- 1) In accordance with DIN 66131
- 2) In accordance with DIN ISO 787/XI, JIS K 5101/18 (not screened)
- 3) In accordance with DIN ISO 787/II, ASTM D 280, JIS K 5101/21
- 4) In accordance with DIN 55921, ASTM D 1208, JIS K 5101/23
- 5) In accordance with DIN ISO 787/IX, ASTM D 1208, JIS K 5101/24
- 6) In accordance with DIN ISO 787/XVIII, JIS K 5101/20
- 7) Referred to the substance dried for 2 hours at 105°C
- 8) Referred to the substance calcined for 2 hours at 1000°C
- 9) Special moisture-resistant packaging
- 10) In water: ethanol 1 : 1
- 11) HCl content in constituent of the loss on ignition

To prepare the silicon dioxides, a liquid silicon compound is sprayed into an oxyhydrogen flame consisting of hydrogen and air. In most cases silicon tetrachloride is used. This substance is hydrolysed to silicon dioxide and hydrochloric acid by the action of the water formed during the hydrogen-oxygen reaction. After leaving the flame, the silicon dioxide enters a so-called coagulation zone, wherein the primary Aerosil particles and primary Aerosil aggregates agglomerate. The product, which exists at this stage as a kind of aerosol, is separated from the accompanying gaseous substances in cyclones and then aftertreated with moist heated air.

By this process the residual hydrochloric acid content can be lowered to 0.025%. As the silicon dioxide obtained at the end of this process has a bulk density of only about 15 g/l, there is a subsequent vacuum compaction, whereby tamped densities of about 50 g/l and more can be established.

20

The particle sizes of the silicon dioxides can be varied by means of the reaction conditions such as, for example, flame temperature, proportions of hydrogen and oxygen, quantity of silicon tetrachloride, residence time in the flame or length of the coagulation path.

The BET surface area is determined using nitrogen in accordance with DIN 66 131.

The pore volume is calculated from the sum of the micro-, meso- and macropore volumes. The micro- and mesopores are determined by recording an N₂ isotherm and evaluation thereof by the methods of BET, de Boer and Barrett, Joyner and Halenda. The macropores $D > 30$ nm are determined by the Hg porosimetry method. For the determination of the macropores, the sample is dried for 15 h at 100°C in the drying oven and degassed at room temperature in a vacuum.

For the determination of the micro- and mesopores, the sample is dried for 15 h at 100°C in the drying oven and degassed for 1 h at 200°C in a vacuum.

- 5 The silanol group concentration is determined by the lithium alanate method. Here the SiOH- groups are reacted with LiAlH₄ and the quantity of hydrogen formed during this reaction is determined from the pressure.

10 Principle of measurement

- The granular material is weighed into a four-necked flask. The flask is evacuated and an oil bath is heated to 150°C. The temperature in the flask (controlled by an internal
15 thermometer) rises with the temperature of the oil bath to about 130°C. The pressure during the preliminary treatment is recorded using a pressure measuring device PI₂ (TM 210, from Leybold, measuring range 10³ to 10⁻³ mbar). The desorption of the water can be monitored from the pressure
20 measurement. At the end of the preliminary treatment (30 min at the end temperature) a pressure of less than 10⁻² mbar must have been achieved.

- After completion of the preliminary treatment, the
25 evacuated flask is separated from the vacuum unit by closing the stop valve and is brought to normal temperature. The actual measurement is based on a measured quantity of LiAlH₄ solution being introduced into the flask through the dropping funnel and the rise in pressure being
30 measured from the hydrogen formed. If the volume of the flask is known, the quantity of H₂ can be calculated from the ideal gas law. The pressure is recorded using a digital measuring device (PI₁) (MKS Instruments PR-2000), having a measuring range of between 0 and 1 bar.

35

The LiAlH₄ solution used (2% LiAlH₄ in diethylene glycol dimethyl ether) is degassed prior to the experiment being

carried out, in order to remove readily volatile constituents, which distort the pressure measurement. For this purpose the pressure above the solution in the dropping funnel is lowered by a second vacuum pump to the vapour pressure (3.7 mbar at 22°C), so that the liquid boils. A blank measurement without a sample is taken to test whether the solution is sufficiently degassed. In the determination of the hydrogen pressure, a correction is made using the vapour pressure of the solvent.

10

Interpretation

The apparatus is calibrated by first of all determining the volume of the dropping funnel provided with a ground-glass stopper, gauging the capacity in litres. The volume of the reaction flask inclusive of all connections as far as the stop valve is obtained by the following experiment:

The dropping funnel, filled with air at atmospheric pressure, is attached to the evacuated flask. A pressure compensation between the two volumes is then brought about by opening the tap of the dropping funnel. The pressure established is indicated by the digital measuring device. The volume of the reaction vessel is obtained from the mass balance. A volume V_R equal to 243.8 ml is obtained with the present arrangement.

The number of moles of hydrogen formed is obtained from the equations:

30

$$n = \frac{p \cdot V(\text{corr.})}{RT}$$

35

$$V_{\text{corr.}} = V_R - V_{\text{solids}} - V_{\text{solution}}$$

p is the increase in pressure in the reaction flask. This value is corrected by an amount corresponding to the vapour pressure of the solvent (3.7 mbar at 22°C). At room temperatures greatly differing from 22°C the vapour pressure is taken from the vapour pressure table. It is useful so to select the weighed sample, that a value for p of between 200 and 800 mbar is obtained. In this case minor changes in the vapour pressure owing to temperature variations have hardly any effect on the result.

10

The volume of the reaction vessel is corrected by deducting the volume of solid matter and the volume of the solution introduced. The former is given from the weighed portion and the density and the latter is read from the dropping funnel.

15

The density of silanol groups is finally obtained from the equation:

20

$$d = \frac{n \cdot N_L}{F}$$

N_L : Lohschmidt number

25 F: Surface of the weighed solid matter

The samples are treated as follows:

1 h heating at 120°C and 0.2 mbar; cooling to 60°C;
30 addition of LiAlH_4 ; after 10 mins, reading the pressure difference which has arisen.

The particle size distribution is determined by means of the laser optical particle size analyser Cilas Granulametre
35 715.

The tapped volume is determined in accordance with ASTM D 4164-88.

Equipment: Tapping volumeter STA V 2003 from
Engelsmann, in accordance with DIN 53194,
section 5.2. b-f
Measuring cylinder 250 ml, graduation marks
every 2 ml
Balance with limit of error of max. ± 0.1 g

Procedure

The counter of the tapping volumometer is set to 1000 strokes.

15 The measuring cylinder is tared.

The granular material is placed in the measuring cylinder up to the 250 ml mark.

The weight of the sample is recorded (± 0.1 g).

20 The measuring cylinder is placed in the volumeter and the apparatus is switched on.

End of tapping: the apparatus automatically switches off after 1000 strokes

The tapped bulk volumes are read to an accuracy of 1 ml.

25 Calculation

E: weighed portion of granular material in g

V: volume read in ml

30 W: water content in wt.% (determined in accordance with Specification P001)

$$\text{Tapped density} = \frac{E \times (100 - W)}{V \times 100}$$

35 The pH value is determined in 4% aqueous dispersion, in the case of hydrophobic catalyst supports in water:ethanol 1:1.

Preparation of the granules according to the invention

The pyrogenically prepared silicon dioxide is dispersed in completely demineralised water. A dispersing aggregate
5 which operates according to the rotor/stator principle is used in the process. The suspensions formed are spray dried. The finished product is precipitated by a filter or cyclone.

10 The sprayed granules are heated in a muffle furnace.

The spray-dried and optionally heated granules are placed in a mixer for the silanisation process and sprayed with intensive mixing optionally first of all with water and
15 then with the silane Si 108 (trimethoxyoctylsilane) or HMDS (hexamethyldisilazane). After spraying has been completed, the material is mixed for 15 to 30 more minutes and then heated for 1 to 4 h at 100 to 400°C.

20 The water used can be acidified with an acid, for example, hydrochloric acid, to a pH value of 7 to 1. The silanising agent used can be dissolved in a solvent such as, for example, ethanol.

Example	Comparison 1	2	3	4	Comparison 5
Starting Aerosil	380	380	380	380	380
Data for spray drying					
Quantity of H ₂ O (kg)	10	10	105	105	15
Quantity of Aerosil (kg)	1.5	1.5	14.7	14.7	1.5
Atomisation using	Disc	Disc	Disc	Disc	Disc
Operating temperature (°C)	380	380	380	440	380
Exhaust air temperature (°C)	105	105	105	108	105
Precipitation	Filter	Filter	Filter	Filter	Cyclone
Data for heating (h/°C)	-	-	2/700	2/700	-
Data for the modification of the surface					
Reagent	-	Si 108	Si 108	HMDS	-
Quantity [g/100 g Aerosil]	-	25	25	20	-
Quantity of water [g/100 g Aerosil]	-	-	5	5	-
Heating time (h)	-	2	2	4	-
Temperature (°C)	-	120	120	140	-
Physicochemical properties					
BET surface area (m ² /g)	350	197	189	212	277
Pore volume (ml/g)	2.09	1.69	1.55	1.68	1.69
Pore volume (% of total pore volume) in pores < 5 nm	n.d.	1.8	n.d.	n.d.	n.d.
Mesopores 2-30 nm (ml/g)	1.34	1.04	1.12	1.17	0.66
Makropores > 30 nm (ml/g)	0.75	0.65	0.43	0.51	1.03
Particle size d ₅₀ (µm)	38	40	66	53	39
Tapped volume (g/l)	320	390	420	370	260
pH value	4.7	5.0	5.6	7.2	4.8
Carbon content %	-	10.9	10.4	3.8	-
Silanol group concentration (mmol OH/g)	1.80	1.18	0.74	0.37	1.50

<i>Example</i>	6	7	8	Comparison 9	10
Starting Aerosil	300	300	300	0 x 50	0 x 50
Data for spray drying					
Quantity of H ₂ O (kg)	15	105	105	10	10
Quantity of Aerosil (kg)	1.5	14.7	14.7	1.5	1.5
Atomisation using	Disc	Single nozzle	Double nozzle	Disc	Disc
Operating temperature (°C)	380	440	440	380	380
Exhaust air temperature (°C)	105	108	108	105	105
Precipitation	Cyclone	Filter	Filter	Cyclone	Cyclone
Data for heating (h/°C)			2/700		
Data for the modification of the surface					
Reagent	HMDS	Si 108	HMDS	-	HMDS
Quantity [g/100 g Aerosil]	15	25	20	-	3
Quantity of water [g/100 g Aerosil]	5	5	5	-	-
Heating time (h)	4	2	4	-	5
Temperature (°C)	140	120	140	-	140
Physicochemical properties					
BET surface area (m ² /g)	222	180	195	46	41
Pore volume (ml/g)	1.79	1.49	1.51	0.73	0.68
Pore volume (% of total pore volume) in pores < 5 nm	n.d.	1.7	1.5	n.d.	1.2
Mesopores 2-30 nm (ml/g)	0.78	0.60	0.60	0.08	0.09
Makropores > 30 nm (ml/g)	1.01	0.89	0.91	0.65	0.59
Particle size d ₅₀ (µm)	32	40	43	21	21
Tapped volume (g/l)	290	320	300	540	570
pH value	6	5.2	6.9	5.3	7.4
Carbon content %	2.7	9.3	3.3	-	0.5
Silanol group concentration (mmol OH/g)	0.61	1.15	0.40	0.29	0.14

<i>Example</i>	<i>Comparison 11</i>	<i>12</i>	<i>Comparison 13</i>	<i>14</i>
Starting Aerosil	130	130	200	200
Data for spray drying				
Quantity of H ₂ O (kg)	15	115	15	15
Quantity of Aerosil (kg)	1.5	1.5	1.5	1.5
Atomisation using	Disc	Disc	Disc	Disc
Operating temperature (°C)	380	380	380	380
Exhaust air temperature (°C)	105	105	105	105
Precipitation	Cyclone	Cyclone	Cyclone	Cyclone
Data for heating (h/°C)	-	-	-	-
Data for the modification of the surface				
Reagent	-	HMDS	-	HMDS
Quantity [g/100 g Aerosil]	-	5	-	7
Quantity of water [g/100 g Aerosil]	-	-	-	-
Heating time (h)	-	5	-	5
Temperature (°C)	-	140	-	140
Physicochemical properties				
BET surface area (m ² /g)	131	111	196	153
Pore volume (ml/g)	1.92	1.62	2.25	2.04
Pore volume (% of total pore volume) in pores < 5 nm	n.d.	1.7	n.d.	0.9
Mesopores 2-30 nm (ml/g)	0.24	0.24	0.46	0.47
Makropores > 30 nm (ml/g)	1.68	1.38	1.79	1.57
Particle size d ⁵⁰ (µm)	20	20	14	14
Tapped volume (g/l)	250	280	230	240
pH value	4.8	7.3	4.8	7.2
Carbon content %	-	1.3	-	1.7
Silanol group concentration (mmol OH/g)	0.83	0.44	1.16	0.56

The particle size distributions of the granules obtained according to Examples 1 to 14 are represented in tabular and graphical form in Figures 1 to 4.

- 5 Examples 1, 5, 9, 11 and 13 are comparative Examples from prior art (DE-A 36 11 449 Liu).

10 Examples of the use of the granules according to the invention as catalyst supports in the production of polyethylene

Referred to the active component titanium, the catalysts achieved the following results in the polymerisation of ethylene:

15

Catalyst on a support Example	Yield kg PE/g Ti	Comment
Example 1	292	Only spray-dried support as in Example 1
Example 2	360	Chemically treated support as in Example 4
Example 3	376	Heat-treated and chemically treated support as in Example 6



28 MAY 1996

Date

Claims

1. Granules based on pyrogenically prepared silicon dioxide and having the following physicochemical properties:

5
Average grain size: 10 to 120 μm
BET surface area: 40 to 400 m^2/g
Pore volume: 0.5 to 2.5 ml/g
10 Pore size distribution: less than 5 % of the total pore volume exists of pores with a diameter < 5 nm, rest meso- and macropores
pH value: 3.6 to 8.5
15 Tapped density: 220 to 700 g/l

2. Method for the preparation of the granules according to claim 1, characterised in that pyrogenically prepared silicon dioxide is dispersed in water and spray dried and the granules obtained are heated at a temperature of from 150 to 1,100°C for a period of 1 to 8 h.

3. Granules based on pyrogenically prepared silicon dioxide and having the following physicochemical properties:

25
Average grain size: 10 to 120 μm
BET surface area: 40 to 400 m^2/g
30 Pore volume: 0.5 to 2.5 ml/g
Pore size distribution: less than 5 % of the total pore volume exists of pores with a diameter < 5 nm, rest meso- and macropores
pH value: 3.6 to 8.5
35 Tapped density: 220 to 700 g/l



4. Method for the preparation of the granules according to claim 3, characterised in that pyrogenically prepared silicon dioxide is dispersed in water and spray dried and the granules obtained are silanised.
5. Granules based on pyrogenically prepared silicon dioxide and having the following physicochemical properties:
- | | | |
|----|-------------------------|--|
| 10 | Average grain size: | 10 to 120 μm |
| | BET surface area: | 40 to 400 m^2/g |
| | Pore volume: | 0.5 to 2.5 ml/g |
| | Pore size distribution: | less than 5 % of the total pore volume exists of pores with a diameter < 5 nm, rest meso- and macropores |
| 15 | pH value: | 3.6 to 8.5 |
| | Tapped density: | 220 to 700 g/l |
- 20 6. Method for the preparation of the granules according to claim 5, characterised in that pyrogenically prepared silicon dioxide is dispersed in water and spray dried and the granules obtained are heated at a temperature of from 150 to 1,100°C for a period of 1 to 8 h and subsequently silanised.
- 25
7. Method for the preparation of granules based on pyrogenically prepared silicon dioxide according to claims 1, 3 and 5, characterised in that pyrogenically prepared silicon dioxide, preferably silicon dioxide prepared from silicon tetrachloride by means of flame hydrolysis, is dispersed in water, spray dried, the granules obtained are optionally heated at a temperature of from 150 to 1,100°C for a period of 1 to 8 h and/or silanised.
- 30
- 35



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8. Use of the granules according to claims 1, 3 and 5 as catalyst supports, in particular for the production of polymerisation catalysts.
- 5 9. Use of the granules according to claims 1, 3 and 5 as catalyst supports for producing catalysts for the production of polyethylene.

Granules based on pyrogenically prepared
silicon dioxide, method for their preparation and
use thereof

5

Abstract

Granules based on silicon dioxide and having the
10 properties:

- Average grain size: 10 to 120 μm
BET surface area: 40 to 400 m^2/g
Pore volume: 0.5 to 2.5 ml/g
15 Pore size distribution: less than 5 % of the total pore
volume exists of pores with a
diameter < 5 nm, rest meso- and
macropores
pH value: 3.6 to 8.5
20 Tapped density: 220 to 700 g/l

They are prepared by dispersing silicon dioxide in water,
spray drying, optionally heating and/or silanising.

25 The granules are used as catalyst supports.

'No Figure Suggested'

Particle size distribution
Si oxide support

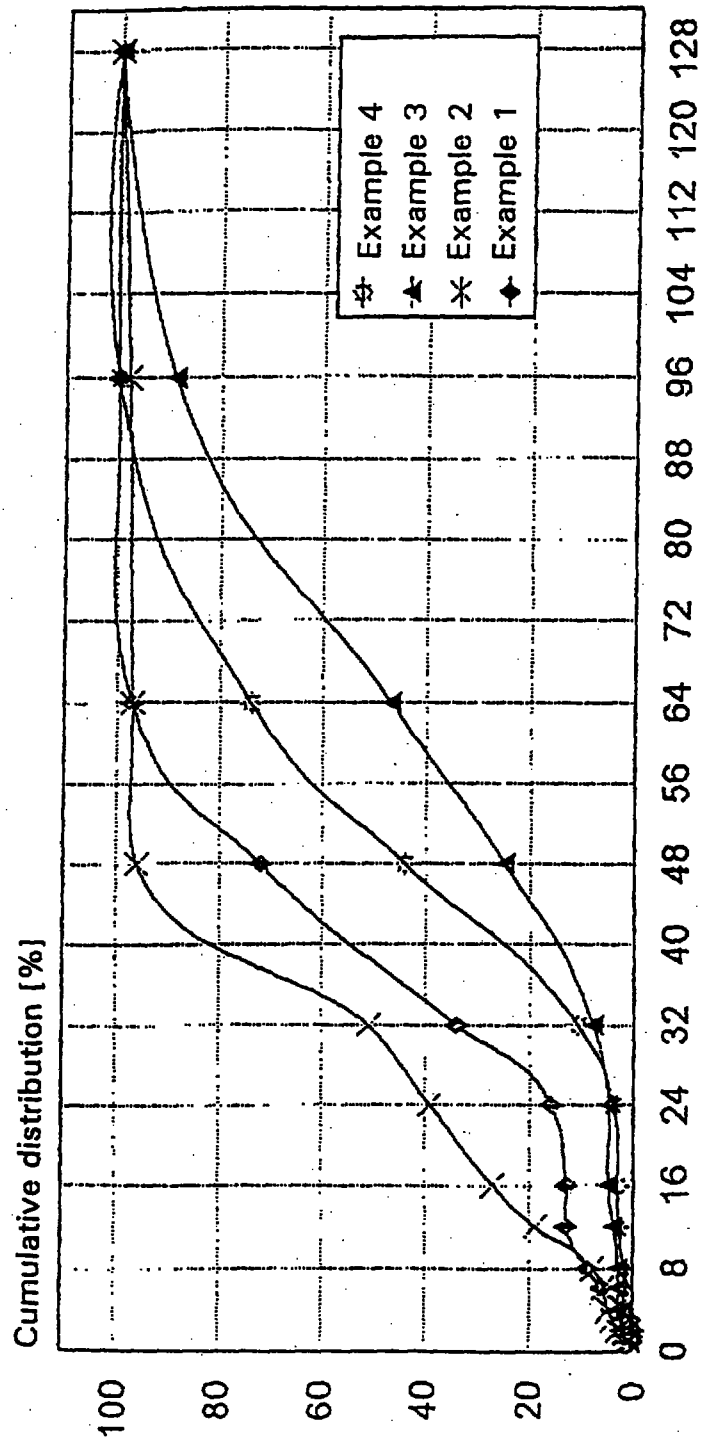


Fig. 1

		particle size																			
		1	1,5	2	3	4	6	8	12	16	24	32	48	64	96	128	[μm]				
Example 1	0	0	0	0	0,4	2	6	9	13	13	16	34	72	97	100	100	100	[%]			
Example 2	1	2	3	4	5	6	6	8	19	27	39	51	96	97	98	100	100	[%]			
Example 3	0,4	0,6	0,8	2	3	3	3	3	4	5	5	8	25	47	89	100	100	[%]			
Example 4	2	2	2	2	2	2	2	2	3	3	4	11	44	74	100	100	100	[%]			

Particle size distribution Si oxide support

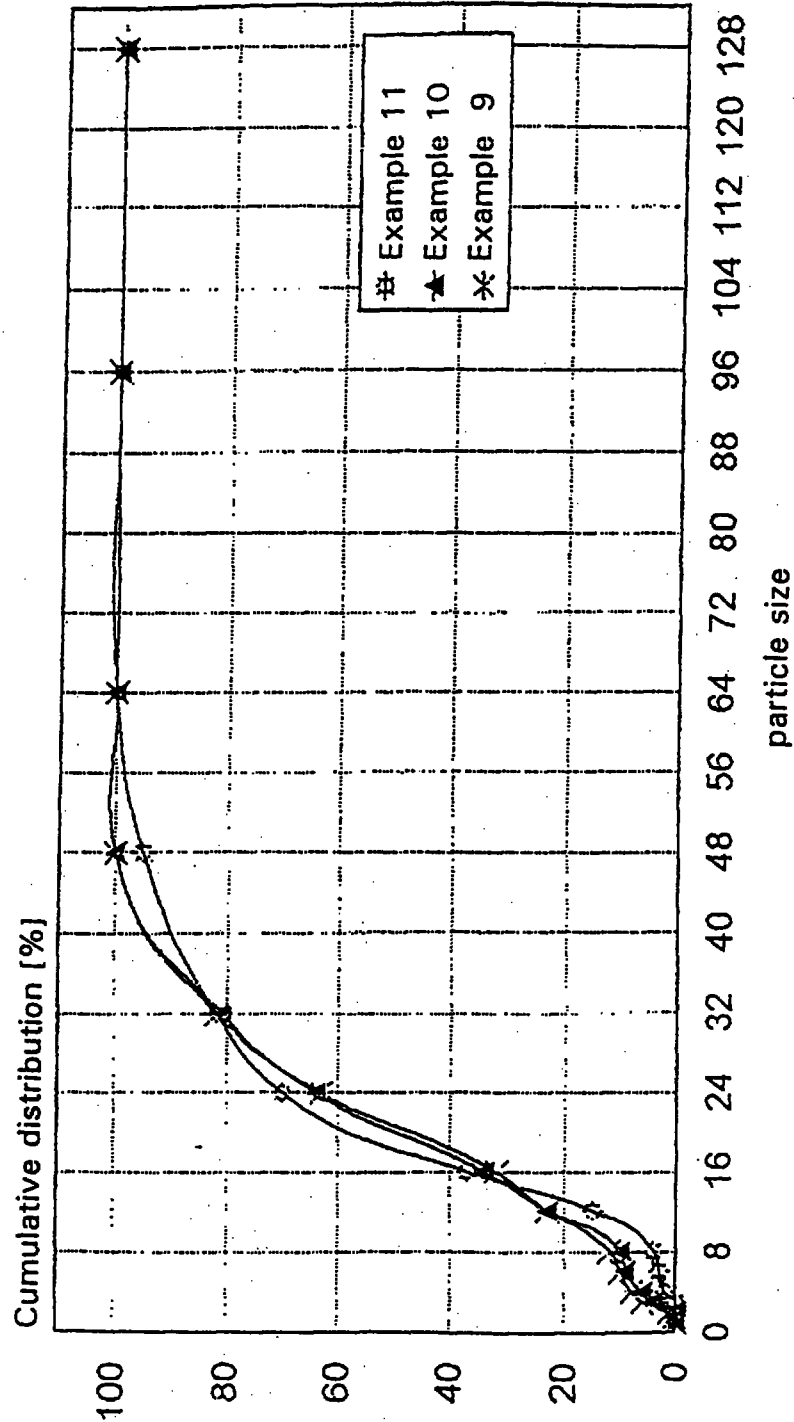


Fig. 2

		particle size																			
		1	1,5	2	3	4	6	8	12	16	24	32	48	64	96	128					
Example 9	0,1	0,1	0,1	1	6	8	10	12	23	32	63	82	100	100	100	100	[μm]				
Example 10	0	0	0,1	4	6	9	10	10	23	34	64	81	100	100	100	100	[%]				
Example 11	0	0	0	0	2	3	4	4	15	37	70	82	95	100	100	100	[%]				

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Particle size distribution Si oxide support

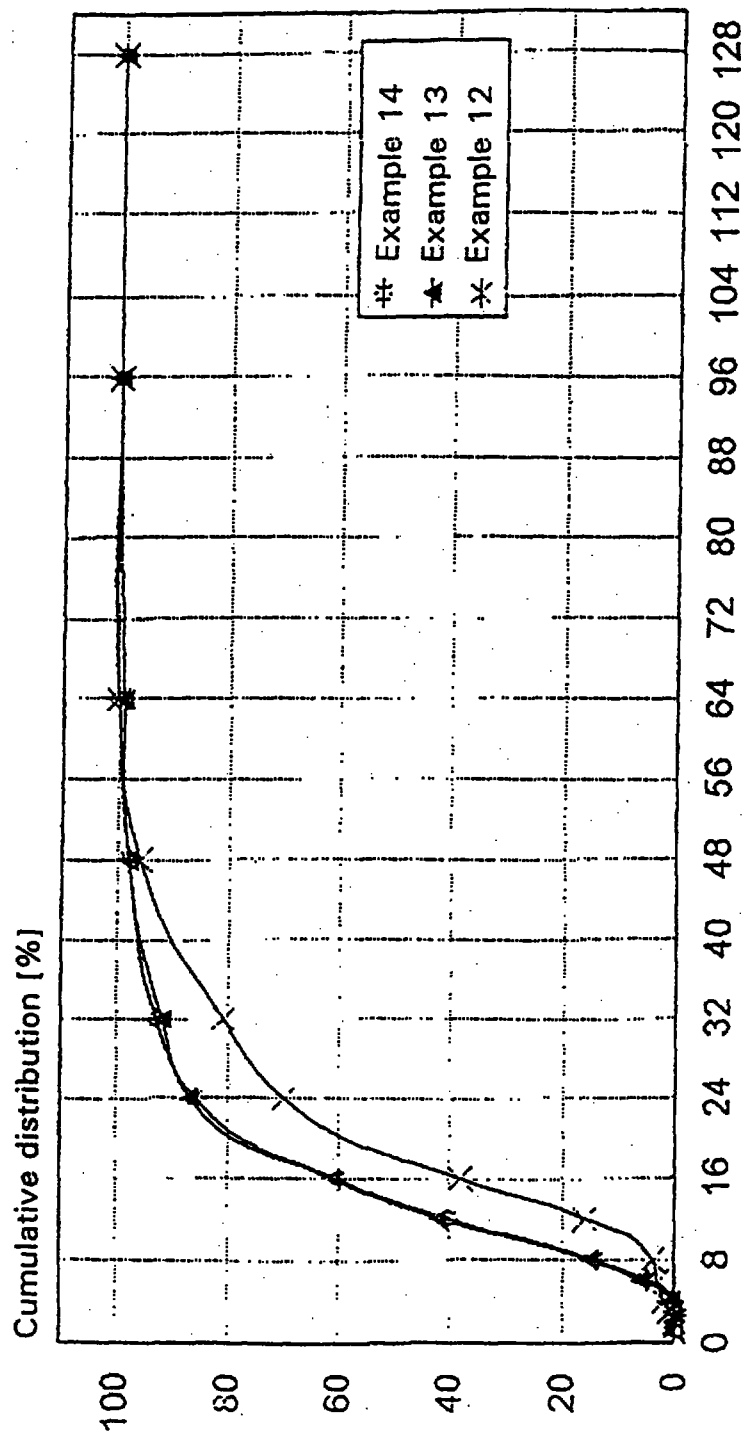


Fig. 3

	particle size																		
	1	1,5	2	3	4	6	8	12	16	24	32	48	64	96	128	[μm]	[%]	[%]	[%]
Example 12	0	0	0	1	2	3	4	16	38	70	81	96	100	100	100				
Example 13	0	0	0	0	0,5	6	15	42	61	87	92	98	99	100	100				
Example 14	0	0	0	0	0	5	14	40	60	86	93	98	100	100	100				

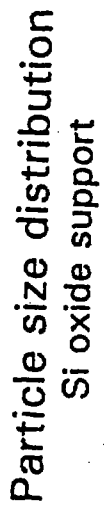


Fig. 4