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(54) PROCESS FOR THE PREPARATION OF GLOBULAR SILICA PARTICLES

(71) We, SHELL INTERNATIONALE RE-
SEARCH MAATSCHAPPIJ B.V., a company
organized under the laws of the Netherlands,
of 30 Carel van Bylandtlaan, The Hague, the
Netherlands, do hereby declare the inven-
tion, for which we pray that a patent may be
granted to us, and the method by which it is
to be performed, to be particularly described
in and by the following statement:—

10 The present invention is concerned with a
process for the preparation of globular silica
particles having a high bulk crushing
strength and water resistivity.

15 Silica particles are applied on a large
scale, for example, as catalysts, catalyst car-
riers, adsorbents, drying agents and ion ex-
changers. For most of these applications
globular particles of uniform shape with a
high bulk crushing strength are preferred.
20 An attractive way to prepare such particles
is the well-known sol-gel method. Accord-
ing to this method a silica hydrosol is pre-
pared by mixing an aqueous solution of an
alkali metal silicate with an aqueous solu-
25 tion of an acid. The hydrosol is converted
into droplet form and the droplets are gelled
in a liquid which is not miscible with water.
After the alkali metal content of the globular
silica hydrogel particles has been reduced in
30 an aqueous medium to less than 1 %w cal-
culated on dry material, they are dried and
calcined.

35 The expression "particles with a high bulk
crushing strength" is used herein to mean
particles having a bulk crushing strength of
at least 12 kg/cm². According to the sol-gel
method silica particles having such a high
bulk crushing strength can easily be ob-
tained. They show, however, a low water
40 resistivity. This is a serious drawback if the
silica particles are to be used for applica-
tions in which they have to be contacted
with water, e.g. for the preparation of silica-
based catalysts by impregnation of the silica
45 particles with an aqueous solution of com-

pounds of catalytically active metals. Upon
contacting the silica particles having a low
water resistivity with water, a considerable
proportion of the particles show cracks or
disintegrates.

50 The expression "particles with a high
water resistivity" used in this patent applica-
tion refers to particles having a water resist-
ivity of at least 80%. The water resistivity
55 of the globular silica particles is determined
in a standard test in which 100 of the globu-
lar silica particles are contacted for 5
minutes at room temperature with a volume
of water which amounts to 5 times the
60 volume of the 100 globular silica particles.
Thereafter the particles are inspected to de-
termine the number of particles which show
cracks or have disintegrated. The water
resistivity of the globular silica particles is
65 expressed as the percentage of particles
which have not been damaged by the contact
with water.

70 It has now been found that globular silica
particles having a high water resistivity can
be prepared according to the sol-gel method,
if at least 25% of the amount (by weight) of
water present in the silica hydrogel particles
is removed therefrom by evaporation before
their alkali metal content is decreased. It is
75 very surprising that a water removal step at
this point in the preparation procedure is
capable of improving the water resistivity
of the ultimate silica particles, the more so
as this water removal step is followed by a
80 step which is carried out in an aqueous
medium and the preparation procedure com-
prises a final, water-removal step. It appears
essential that the aforesaid water removal
step be carried out before the alkali metal
85 content of the particles is decreased, and
that the beneficial effect of this water re-
moval step on the water resistivity of the
ultimate silica particles is not affected ad-
versely by the subsequent treatment of the
90 particles in an aqueous medium.

The expression "water removal by evaporation" is used herein to distinguish the present water-removal treatment from other treatments by which water is removed from silica hydrogels such as a treatment of the silica hydrogel particles with an aqueous solution of ammonia. It has been found that the latter treatment is capable of improving the water resistivity of the ultimate globular silica particles, but not to a degree sufficient to increase the water resistivity of the particles beyond the required 80% level. A serious drawback of this treatment, which makes it completely unsuitable for the present purpose is that as a result of this treatment the bulk crushing strength of the particles decreases dramatically to far below the required level of 12 kg/cm².

According to the present invention a process for the preparation of globular silica particles, comprises the following successive steps:

- (a) preparing a silica hydrosol by mixing an aqueous solution of an alkali metal silicate with an aqueous solution of an acid,
- (b) converting the hydrosol into droplet form,
- (c) gelling the droplets in a liquid which is not miscible with water,
- (d) removing at least 25% of the amount (by weight) of water present in the hydrogel particles by evaporation,
- (e) decreasing the alkali metal content of the hydrogel particles in an aqueous medium to less than 1%w calculated on dry material; and
- (f) drying and calcining the globular silica particles.

In addition to the possibility of preparing globular silica particles having a high water resistivity by the sol-gel method, the incorporation of the present water removal step has a cost-saving effect, since smaller volumes of material have to be handled in the successive steps of the process.

In the process according to the invention, first of all a silica hydrosol is prepared by mixing an aqueous solution of an alkali metal silicate with an aqueous solution of an acid. This may very suitably be performed by leading the starting solutions separately into a mixing chamber where mixing of the solutions takes place by stirring. As alkali metal silicate and as acid, sodium silicate and sulphuric acid, respectively, are very suitable. After the silica hydrosol has been formed it is converted into droplet form and gelled in a liquid which is not miscible with water. This may very suitably be performed by introducing the hydrosol via a small aperture in the bottom of the mixing chamber into the upper end of a vertically disposed tube filled with oil. Gelation occurs while the hydrosol droplets move downwards

through the oil. At the bottom of the tube the globular hydrogel particles may be caught in water, separated from the water e.g. by filtration, washed with water and thereafter subjected to the water removal step. It is also possible to carry out the water removal step in the same oil wherein gelation has taken place.

In the water removal step according to the invention at least 25% and preferably at least 50% of the amount (by weight) of water present in the hydrogel particles is removed therefrom by evaporation. This water removal step may be carried out in various ways. Water may e.g. be removed from the hydrogel particles by contacting them with a dry gas stream, e.g. a stream of dry air either or not at elevated temperature. Water may also be removed from the hydrogel particles by heating them at atmospheric pressure or at reduced or elevated pressure. Other ways of removing water from the hydrogel particles are contacting them with an inert liquid (i.e. a liquid which does not react chemically with the hydrogel) at a temperature above 100°C or contacting them at elevated temperature with steam or a steam-containing gas stream. Examples of treatments which may very suitably be applied for removing at least 25% of the water present in the hydrogel particles are the following:

- (a) heating the hydrogel particles at a temperature of about 100°C at reduced pressure,
- (b) heating the hydrogel particles at a temperature above 100°C in a stream of air,
- (c) heating the hydrogel particles at a temperature of about 100°C at reduced pressure followed by heating the particles at a temperature of about 500°C in a stream of air,
- (d) contacting the hydrogel particles with a hydrocarbon oil at a temperature above 100°C,
- (e) heating the hydrogel particles at a temperature above 100°C in an autoclave at autogeneous pressure, and
- (f) heating the hydrogel particles in a stream of air and steam.

After the treating step in which at least 25% of the water present in the hydrogel particles is removed therefrom by evaporation, the alkali metal content of the hydrogel particles is decreased in an aqueous medium to less than 1%w calculated on dry material. This alkali metal removal may very suitably be performed by treating the hydrogel particles with an aqueous solution of ammonium nitrate until the desired low alkali metal content has been reached.

Finally the hydrogel particles are dried and calcined. Drying and calcining of the hydrogel particles may e.g. be carried out by

heating the particles for a certain period of time at a temperature of 100–200°C and 450–550°C, respectively.

5 If desired, a small amount of a filler may be incorporated into the silica particles according to the invention. Incorporation of a filler may be attractive for various reasons. In the first place the porosity of the ultimate silica particles may be influenced by this measure. Further, for certain applications of the silica particles, the presence of e.g. an alumina filler therein may be attractive. It is also possible to decrease the cost of preparation of the silica particles by incorporating therein a cheap filler. The incorporation of the filler into the silica particles may very suitably be performed by adding the filler to the aqueous solution of the alkali metal silicate and/or to the aqueous solution of the acid from which the hydrosol is prepared by mixing. Examples of suitable fillers are kaolin, montmorillonite, bentonite, precipitated silica fillers, aluminas, zeolites and amorphous precipitated silica-aluminas.

25 With respect to the amount of filler which may be incorporated into the silica particles according to the invention, it has been found that the presence of a filler in the ultimate silica particles reduces the bulk crushing strength of the particles, which effect is more pronounced according as the filler content of the particles is higher. Since, however, the sol-gel method as a rule provides globular silica particles with a very high bulk crushing strength, a small decrease is of no importance, and filler containing globular silica particles which amply comply with the requirement that the bulk crushing strength should amount to at least 12 kg/cm² can be easily prepared, provided that the quantity of filler incorporated therein amounts to not more than 25% of the quantity of silica present in the hydrosol from which the silica particles are prepared. Incorporation of larger amounts of filler in the silica particles entails the risk that silica particles with a bulk crushing strength below 12 kg/cm² are obtained, and therefore falls outside the scope of the present patent application.

50 Globular silica particles prepared according to the present invention may be applied e.g. as catalysts, catalyst carriers, adsorbents, drying agents and ion exchangers. They are of particular importance as carriers for one or more metals with catalytic activity. Catalysts comprising the present silica particles as carrier may be applied in various processes in the chemical and petroleum industries. The preparation of the catalysts may be carried out by any technique for the preparation of supported catalysts known in the art, e.g. by impregnating the globular silica particles with an aqueous solution comprising salts of the catalytically active metals concerned, followed by drying and

calcining of the composition. An attractive way of preparing the present catalysts is one in which the catalytically active metals are incorporated into the carrier in an early stage of the carrier preparation, e.g. when the latter is still in the hydrogel form. Not only can the porosity of the ultimate catalyst be influenced, but also this method of preparation offers the advantage that the additional drying and calcining steps required after impregnation become superfluous.

Globular silica particles prepared according to the invention are of particular importance as carriers for catalysts which are used in the hydrometallization of heavy hydrocarbon oils and in the epoxidation of olefinically unsaturated compounds with an organic hydroperoxide.

Hydrometallization of heavy hydrocarbon oils is a well-known process in the petroleum industry and is applied, amongst other things, to decrease the metal content of heavy hydrocarbon oils which are to be used as feed for catalytic treating processes such as hydrosulphurization or catalytic conversion processes such as hydrocracking and catalytic cracking. As a result of the demetallization, the life of the catalyst in the subsequent treating or conversion process is prolonged. Hydrometallization is carried out by contacting the heavy hydrocarbon oil at elevated temperature and pressure in the presence of hydrogen with a catalyst. Preferred catalysts for this purpose are catalysts comprising one or more metals selected from nickel, cobalt, molybdenum, tungsten and vanadium on a silica carrier. Especially preferred are catalysts comprising at least one metal selected from nickel and cobalt and at least one metal selected from molybdenum, tungsten, and vanadium, such as the metal combination nickel/vanadium, nickel/molybdenum and cobalt/molybdenum on a silica carrier. Globular silica particles prepared according to the present invention are preferred carriers for these catalysts.

The catalytic epoxidation of an olefinically unsaturated compound with an organic hydroperoxide can be used, for example, for the preparation of propylene oxide and epichlorohydrin from propylene and allyl chloride, respectively. The epoxidation of an olefinically unsaturated compound with an organic hydroperoxide can be carried out by contacting the reactants in the liquid phase and at elevated temperature and (depending on the olefinically unsaturated compound) pressure with a catalyst. As organic hydroperoxide ethyl benzene hydroperoxide is preferred, since the methylphenylcarbinol which is obtained as a by-product in the reaction may easily be converted into valuable styrene. Preferred catalysts for the epoxidation are catalysts comprising a com-

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pound of at least one metal selected from molybdenum, tungsten, titanium, zirconium and vanadium. Especially preferred are heterogeneous catalysts comprising titanium in chemical combination with silicon and oxygen, the catalytically active component being supported on a silica carrier. Globular silica particles prepared by the process of the present invention are preferred carriers for use in preparing these heterogeneous catalysts.

The present invention is illustrated by the following examples, which also include some comparative examples:

15 Comparative Example A

20 An aqueous sodium waterglass solution comprising 12%w SiO_2 and having a $\text{Na}_2\text{O}/\text{SiO}_2$ molar ratio of 0.3 was mixed continuously in a mixing chamber with an aqueous 1.2 N sulphuric acid solution in a volume ratio acid solution/waterglass solution of 0.75. After a residence of a few seconds in the mixing chamber the hydrosol obtained was converted into droplet form and the hydrosol droplets allowed to fall through a vertically disposed cylindrical tube with a length of 1.8 m filled with a paraffinic hydrocarbon oil at 25°C. During the fall through the tube gelation occurred. The globular hydrogel particles were caught at the bottom of the tube in water at 25°C. After the globular hydrogel particles had been separated by filtration they were washed with water. The water content of these globular hydrogel particles was determined in a standard test in which a sample was heated in three hours from room temperature to 600°C and thereafter kept at 600°C for one hour. The water content of the hydrogel particles appeared to be 90%w. Water contents of silica hydrogel particles mentioned in the following examples have all been determined by the above-described standard test.

45 Comparative Example B

50 A portion of the silica hydrogel particles with a water content of 90%w prepared according to comparative example A was treated with an aqueous 0.1 M ammonium nitrate solution at room temperature until the sodium content of the particles had been decreased to 0.2%w calculated on dry material. After drying for 2 hours at 100°C and calcining for 3 hours at 500°C the globular silica particles thus obtained showed a water resistivity of 30% and a bulk crushing strength above 16.7 kg/cm². (16.7 kg/cm² is the maximum value which can be measured with the bulk crushing strength determination method applied).

EXAMPLE I

65 A portion of the silica hydrogel particles with a water content of 90 %w prepared according to comparative example A was dried

for 2 hours at 100°C at reduced pressure. After this treatment the water content of the hydrogel particles amounted to 18%w. Subsequently the hydrogel particles were treated with an aqueous solution of ammonium nitrate, dried and calcined in the same way as the hydrogel particles in comparative example B. The globular silica particles thus obtained showed a water resistivity of 95% and a bulk crushing strength above 16.7 kg/cm².

EXAMPLE II

A portion of the silica hydrogel particles with a water content of 90%w prepared according to comparative example A was dried for 3 hours at 120°C in a stream of air. After this treatment the water content of the hydrogel particles amounted to 14 %w. Subsequently the hydrogel particles were treated with an aqueous solution of ammonium nitrate, dried and calcined in the same way as the hydrogel particles in comparative example B. The globular silica particles thus obtained showed a water resistivity of 93% and a bulk crushing strength above 16.7 kg/cm².

EXAMPLE III

A portion of the silica hydrogel particles with a water content of 90%w prepared according to comparative example A was dried for 2 hours at 100°C at reduced pressure and thereafter calcined for 3 hours at 500°C in a stream of air. After this treatment the water content of the particles amounted to 3 %w. Subsequently the particles were treated with an aqueous solution of ammonium nitrate, dried and calcined in the same way as the hydrogel particles in comparative example B. The globular silica particles thus obtained showed a water resistivity of 95% and a bulk crushing strength above 16.7 kg/cm².

EXAMPLE IV

A portion of the silica particles with a water content of 90 %w prepared according to comparative example A was kept in contact with a paraffinic hydrocarbon oil at 150°C for 6 hours. After this treatment the water content of the particles had decreased to 12%w. Subsequently the particles were treated with an aqueous solution of ammonium nitrate dried and calcined in the same way as the hydrogel particles in comparative example B. The globular silica particles thus obtained showed a water resistivity of 96% and a bulk crushing strength above 16.7 kg/cm².

EXAMPLE V

A portion of the silica particles with a water content of 90%w prepared according to comparative example A was heated

for 1½ hours at 185°C at autogeneous pressure in an autoclave. After this treatment the water content of the hydrogel particles amounted to 15%w. Subsequently the hydrogel particles were treated with an aqueous solution of ammonium nitrate, dried and calcined in the same way as the hydrogel particles in comparative example B. The globular silica particles thus obtained showed a water resistivity of 94% and a bulk crushing strength above 16.7 kg/cm².

EXAMPLE VI

This example was carried out substantially in the same way as example I, however, in the present case the aqueous sodium waterglass solution contained 12 g powdered kaolin filler per litre (this corresponds to 10% of the quantity of silica present in the sol). The ultimate globular silica particles showed a water resistivity of 91% and a bulk crushing strength of 15 kg/cm².

EXAMPLE VII

A portion of the silica particles with a water content of 90%w prepared according to comparative Example A was heated for 4 hours at 120°C at autogeneous pressure in an autoclave. After this treatment the water content of the hydrogel particles amounted to 60%w. Subsequently the hydrogel particles were treated with an aqueous solution of ammonium nitrate, dried and calcined in the same way as the hydrogel particles in comparative Example B. The globular silica particles thus obtained showed a water resistivity of 98% and a bulk crushing strength above 16.7 kg/cm².

Comparative Example C

This example was carried out in substantially the same way as example I, however, in the present case the aqueous sodium waterglass solution contained 72 g powdered kaolin filler per litre (this corresponds to 60% of the quantity of silica present in the sol). The ultimate globular silica particles showed a water resistivity of 85% and a bulk crushing strength of 10 kg/cm².

Comparative Example D

A portion of the silica hydrogel particles with a water content of 90 %w prepared according to comparative example A was covered for 16 hours at room temperature with an aqueous solution containing 25% w ammonia. After this treatment the water content of the hydrogel particles amounted to 30%w. Subsequently the hydrogel particles were treated with an aqueous solution of ammonium nitrate, dried and calcined in the same way as the hydrogel particles in comparative example B. The globular silica particles thus obtained showed a water re-

sistivity of 45% and a bulk crushing strength of 5 kg/cm².

Comparative Example E

A portion of the silica particles with a water content of 90%w prepared according to comparative example A was heated for ½ hour at 120°C at autogeneous pressure in an autoclave. After this treatment the water content of the hydrogel particles amounted to 72%w. Subsequently the hydrogel particles were treated with an aqueous solution of ammonium nitrate, dried and calcined in the same way as the hydrogel particles in comparative example B. The globular silica particles thus obtained showed a water resistivity of 50% and a bulk crushing strength of 8 kg/cm².

WHAT WE CLAIM IS:—

1. A process for the preparation of globular silica particles, which comprise the following successive steps:

- (a) preparing a silica hydrosol by mixing an aqueous solution of an alkali metal silicate with an aqueous solution of an acid,
- (b) converting the hydrosol into droplet form,
- (c) gelling the droplets in a liquid which is not miscible with water,
- (d) removing at least 25% of the amount (by weight) of water present in the hydrogel particles by evaporation,
- (e) decreasing the alkali metal content of the hydrogel particles in an aqueous medium to less than 1% calculated on dry material, and
- (f) drying and calcining the globular silica particles.

2. A process as claimed in claim 1, in which at least 50% of the amount (by weight) of water present in the hydrogel particles is removed by evaporation in step (d).

3. A process as claimed in claim 1 or 2, in which water is removed by evaporation from the hydrogel particles in step (d) by contacting them with a dry gas stream.

4. A process as claimed in claim 1 or 2, in which water is removed by evaporation from the hydrogel particles in step (d) by heating them.

5. A process as claimed in claim 1 or 2, in which water is removed by evaporation from the hydrogel particles in step (d) by contacting them with an inert liquid (as herein defined) at a temperature above 100°C.

6. A process as claimed in claim 1 or 2, in which water is removed by evaporation from the hydrogel particles in step (d) by contacting them at elevated temperature with steam or a steam-containing gas stream.

7. A process as claimed in any one of claims 1—6, in which a quantity of filler,



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for 1½ hours at 185°C at autogeneous pressure in an autoclave. After this treatment the water content of the hydrogel particles amounted to 15%w. Subsequently the hydrogel particles were treated with an aqueous solution of ammonium nitrate, dried and calcined in the same way as the hydrogel particles in comparative example B. The globular silica particles thus obtained showed a water resistivity of 94% and a bulk crushing strength above 16.7 kg/cm².

EXAMPLE VI

This example was carried out substantially in the same way as example I, however, in the present case the aqueous sodium waterglass solution contained 12 g powdered kaolin filler per litre (this corresponds to 10% of the quantity of silica present in the sol). The ultimate globular silica particles showed a water resistivity of 91% and a bulk crushing strength of 15 kg/cm².

EXAMPLE VII

A portion of the silica particles with a water content of 90%w prepared according to comparative Example A was heated for 4 hours at 120°C at autogeneous pressure in an autoclave. After this treatment the water content of the hydrogel particles amounted to 60%w. Subsequently the hydrogel particles were treated with an aqueous solution of ammonium nitrate, dried and calcined in the same way as the hydrogel particles in comparative Example B. The globular silica particles thus obtained showed a water resistivity of 98% and a bulk crushing strength above 16.7 kg/cm².

Comparative Example C

This example was carried out in substantially the same way as example I, however, in the present case the aqueous sodium waterglass solution contained 72 g powdered kaolin filler per litre (this corresponds to 60% of the quantity of silica present in the sol). The ultimate globular silica particles showed a water resistivity of 85% and a bulk crushing strength of 10 kg/cm².

Comparative Example D

A portion of the silica hydrogel particles with a water content of 90 %w prepared according to comparative example A was covered for 16 hours at room temperature with an aqueous solution containing 25% w ammonia. After this treatment the water content of the hydrogel particles amounted to 30%w. Subsequently the hydrogel particles were treated with an aqueous solution of ammonium nitrate, dried and calcined in the same way as the hydrogel particles in comparative example B. The globular silica particles thus obtained showed a water re-

sistivity of 45% and a bulk crushing strength of 5 kg/cm².

Comparative Example E

A portion of the silica particles with a water content of 90%w prepared according to comparative example A was heated for ½ hour at 120°C at autogeneous pressure in an autoclave. After this treatment the water content of the hydrogel particles amounted to 72%w. Subsequently the hydrogel particles were treated with an aqueous solution of ammonium nitrate, dried and calcined in the same way as the hydrogel particles in comparative example B. The globular silica particles thus obtained showed a water resistivity of 50% and a bulk crushing strength of 8 kg/cm².

WHAT WE CLAIM IS:—

1. A process for the preparation of globular silica particles, which comprise the following successive steps:
 - (a) preparing a silica hydrosol by mixing an aqueous solution of an alkali metal silicate with an aqueous solution of an acid,
 - (b) converting the hydrosol into droplet form,
 - (c) gelling the droplets in a liquid which is not miscible with water,
 - (d) removing at least 25% of the amount (by weight) of water present in the hydrogel particles by evaporation,
 - (e) decreasing the alkali metal content of the hydrogel particles in an aqueous medium to less than 1% calculated on dry material, and
 - (f) drying and calcining the globular silica particles.
2. A process as claimed in claim 1, in which at least 50% of the amount (by weight) of water present in the hydrogel particles is removed by evaporation in step (d).
3. A process as claimed in claim 1 or 2, in which water is removed by evaporation from the hydrogel particles in step (d) by contacting them with a dry gas stream.
4. A process as claimed in claim 1 or 2, in which water is removed by evaporation from the hydrogel particles in step (d) by heating them.
5. A process as claimed in claim 1 or 2, in which water is removed by evaporation from the hydrogel particles in step (d) by contacting them with an inert liquid (as herein defined) at a temperature above 100°C.
6. A process as claimed in claim 1 or 2, in which water is removed by evaporation from the hydrogel particles in step (d) by contacting them at elevated temperature with steam or a steam-containing gas stream.
7. A process as claimed in any one of claims 1—6, in which a quantity of filler,



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amounting to not more than 25% wt of the quantity of silica present in the hydrosol from which the silica particles are prepared, is incorporated into the silica particles.

5 8. A process for the preparation of globular silica particles as claimed in claim 1 and substantially as described hereinbefore with reference to any one of Examples I—VII.

10 9. Globular silica particles prepared according to the process claimed in any one of the preceding claims.

15 10. Catalysts comprising one or more metals with catalytic activity on globular silica particles according to claim 9 as carrier.

20 11. A process for the preparation of catalysts according to claim 10, in which the catalytically active metals are incorporated into the carrier during the preparation thereof.

25 12. A process for the hydrodemetallization of a heavy hydrocarbon oil in which the heavy oil is contacted at elevated temperature and pressure and in the presence of hydrogen with a catalyst according to claim 10 or 11, which catalyst comprises at least

one metal selected from the group consisting of nickel and cobalt and at least one metal selected from the group consisting of molybdenum, tungsten and vanadium as catalytically active metals.

13. A process for the epoxidation of an olefinically unsaturated compound with an organic hydroperoxide, in which process the reactants in the liquid phase are contacted at elevated temperature and (depending on the olefinically unsaturated compound) pressure with a heterogeneous catalyst which comprises titanium in chemical combination with silicon and oxygen, the catalytically active component being supported on a silica carrier, wherein said catalyst is prepared using globular silica particles as claimed in claim 9.

14. A process as claimed in claim 13, in which the olefinically unsaturated compound is propylene or allyl chloride.

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