

PATENT SPECIFICATION

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DRAWINGS ATTACHED

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(54) PREPARATION OF SILICA GELS

- (71) We, NATIONAL DISTILLERS AND CHEMICAL CORPORATION of 99 Park Avenue, New York, State of New York, United States of America, a corporation organised and existing under the laws of the State of Virginia, United States of America, do hereby declare the invention, 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:—
- This invention relates to silica xerogels and to their preparation.
- Much of the technology in the area of silica gels involves the problem of making strong hard gel masses which will not shrink and crack upon being dried. The gels are useful as absorbents and catalyst bases. Gels of small particle size and narrow particle size distribution, about 50 microns mean diameter, have been found to be the most desirable for fluid bed or stirred reactor catalyst operations because they are more easily fluidized, reduce the amount of erosion of equipment and suffer less degradation by abrasion and particle rupture.
- The only silica gels thus far reported having suitable particle size and narrow particle size distribution for the purposes mentioned above are characterized by a maximum pore volume of 1.8 to 1.9 cm³/g and surface areas of from 250—350 m²/g. Silica gels having higher average pore diameters reported in the prior art have only been obtained as aerogels. Aerogels are subjected to shrinking when they are wet due to coalescence of the ultimate particles. This produces a loss of porosity, and makes the products unsatisfactory for certain uses, especially as polymerization catalysts.
- The present invention provides a method for producing a silica xerogel which comprises 1) forming a silica hydrogel by a) reducing the pH of an aqueous solution of sodium silicate to provide a silica hydrogel slurry having an SiO₂ concentration of from 5 to 12 wt.% and a pH of from 3 to 8, the temperature during precipitation being maintained between 0°C and 10°C, b) heating the product of step a) at a pH of from 3 to 8 and at a temperature of from 50 to 100°C for from 1 to 6 hours, and c) washing the product of step b) to remove sodium until the filtrate contains less than 20 ppm by weight of sodium salt, and 2) converting the hydrogel to a xerogel, by d) replacing the water in the hydrogel by a liquid of lower surface tension e) thereafter drying the gel when a xerogel which has surface area of from 200 to 500 m²/g the majority of which is provided by pores of a diameter of from 300 to 600Å and which has stability at temperatures up to 1100°C in a fluidized bed may be produced.
- The liquid of lower surface tension may be introduced into the gel by dissolution in the water of a surfactant, or by replacing water in the pores with a water-miscible organic liquid such as acetone or an alcohol.
- One preferred method according to the invention comprises the following steps:
1. Precipitation of a silica gel by reducing the pH of aqueous xNa₂O . ySiO₂ with an acid, e.g. H₂SO₄ or CO₂, ion exchange resins, or by other suitable procedure, carried out in stoichiometric proportions under good agitation and in accordance with the following conditions.
 - (a) The SiO₂ concentration in the final slurry is from 5 to 12 per cent by weight and preferably from 8 to 9 per cent,
 - (b) The pH-reducing medium is most advantageously added at the rate of 40 per cent of the needed amount in from 30 minutes to 120 minutes, and preferably about 60 minutes, and the remaining 60 per cent of the amount in from 20 to 90 minutes more, and preferably about 45 minutes more,
 - (c) the temperature during precipitation is maintained between 0 and 10°C and preferably at about 5°C, and
 - (d) The final pH of the precipitate is from 3 to 8 and preferably from 5 to 7.
 2. Heating the precipitated silica hydrogel slurry under the following conditions:
 - (a) A pH of from 3 to 8, and preferably from 5 to 7.

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(b) A temperature from 50 to 100°C, and preferably about 90°C, and

(c) For a period of from 1 to 6 hours and preferably about 4 hours.

5 3. Washing the product with one or more salts having a displacing effect on sodium so that the filtrate titrates less than 20 ppm by weight sodium salt concentration. Suitable salts include aluminum chloride or sulfate and ammonium chloride or nitrate. The displacing can also be accomplished by washing with a strong acid such as hydrochloric acid or H_2SO_4 .

15 4. Reducing the gel particle size by high shear mixing (homogenising) the product from step 3 to obtain particles having a mean diameter of less than 200 microns and preferably of from 30 to 150 microns.

20 5. Displacing the water from the gel by use of a alcohol and/or acetone, or other water-miscible organic compound which can displace water and reduce the surface tension in the pores.

25 6. Drying the gels, e.g. by spray-drying or distilling, and

7. Calcining the product from step 6 at a temperature of from 260 to 650°C. and preferably at about 540°C.

30 Comminution of the precipitated hydrogel to a particle size of less than 200 microns, if this is necessary, can be effected before or after displacement of water therefrom with the organic liquid.

35 The invention will now be described in greater detail with reference to specific examples which illustrate the criticality of process conditions in order to obtain a silica xerogel product having the required properties.

40 The properties of the silica xerogel obtained in accordance with the invention and particularly the porosity characteristics are discussed in terms of pore volume (PV), surface area (SA), average pore diameter (Av. Pd), where

$$45 \quad \text{Av. Pd} = \frac{4PV}{SA},$$

and pore size distribution. Determinations of the values for the various properties are made by a nitrogen absorption-desorption technique well known in the art and described in detail

50 In the following examples, Example I is a description of a preferred method for carrying out the process of the invention to obtain a silica xerogel of the stated characteristics. The remainder of the examples illustrate the criticality of various process conditions or describe suitable alternative procedures for obtaining the silica xerogels.

EXAMPLE I

60 10080 g of sodium silicate solution contain-

ing 28.7% SiO_2 and 8.9% of Na_2O was added to 12,720 g of water and cooled to 5°C under agitation.

11,200 g of H_2SO_4 (12.75 wt.%) was then added as follows:

(a) 4480 g was added at a constant rate over a period of one hour, and

(b) the remainder was added over a period of 45 minutes.

The final pH of the precipitate was 6.2 and the SiO_2 content was approximately 8.5%.

The slurry was then heated to 95°C and held at that temperature for 3 hours. The slurry was washed with a solution of 1113 g of NH_4NO_3 in 45 gallons of water, and then with de-ionized water until the filtrate titrated less than 20 ppm Na_2SO_4 .

The product was re-slurried in acetone and washed with acetone until the water in the acetone titrated less than 1.0% by weight.

The product was then homogenized and the acetone distilled off to reduce the acetone content to less than 1% by weight.

The silica gel obtained was calcined in an oven at 540°C for 4 hours before evaluation. The physical properties of the silica xerogel thus obtained were: SA=268 m^2/g , PV=2.52 cm^3/g , Av. Pd=365Å.

Referring to Figure 1 of the drawing, it will be seen that the major portion of the cumulative surface area of the silica xerogel product is accounted for by pores having a pore diameter in the range of from 300—600Å.

After calcination in a fluidized bed at 983°C for 3 hours, the physical properties were unchanged: SA=278 m^2/g , PV=2.54 cm^3/g , Av. Pd=365Å.

EXAMPLE II

All of the variables during precipitation, except final SiO_2 concentration, were maintained as in Example I. Final SiO_2 concentrations of 7 and 10% were chosen and Figure 2 shows the effect of SiO_2 concentration on the porosity of the gel just after precipitation.

Referring to Figure 2 of the drawing, it will be seen that lower pore volumes are obtained where the final silica concentration in the slurry is 7 and 10% as compared with the pore volume obtained in Example I where an SiO_2 concentration of about 8.5% was obtained. Figure 2 also demonstrates that the surface area increases as the SiO_2 concentration increases. Thus, in order to get maximum pore volume and at the same time obtain a good surface area level it is preferable to maintain the SiO_2 concentration at from 8 to 9% and most preferably at about 8.5%.

EXAMPLE III

All variable during precipitation, except the acid addition rate, were maintained as in

Example I. The initial 40% of the stoichiometric acid requirement was added at constant rate in 0.5 and 2.0 hours as compared to 1.0 hours in Example I.

- 5 Example III clearly illustrates, as shown in Figure 3 of the drawings, that both pore volume and surface area of the precipitated hydrogel are dependent upon the rate at which the pH-reducing medium, in this case the sulfuric acid, is added to the aqueous silicate solution. It will be seen that optimum pore volume and surface area values are obtained using an addition rate of about 1 hour for 40% of the stoichiometric amount and that 10 lower values for pore volume and surface area are obtained where more rapid or slower addition rates are employed.

EXAMPLE IV

- 20 All variable during precipitation, except temperature, were maintained as in Example I. Temperatures of 25°C and 50°C were used during precipitation. Figure 4 shows the effect of temperature on the porosity of the gel just after precipitation.

- 25 As will be seen by reference to Figure 4, the pore volume decreases as the precipitation temperature increases. Surface area also tends to decrease with an increase in the precipitation temperature, but this value flattens out at about 5°C and this is the preferred temperature of precipitation in order to secure optimum values for pore volume and surface area.

EXAMPLE V

- 35 In this example all the variables during precipitation were maintained as in Example I, but CO₂ was used to neutralize the sodium

silicate instead of sulfuric acid. The physical properties of the silica gel were similar to those obtained under Example I.

EXAMPLE VI

All the variables during precipitation were maintained the same as in Example I. After precipitation, the gel was adjusted to a pH of 9.0 by adding NaOH (2-normal) and was heated for one hour at 95°C. The gel was then washed as in Example I before evaluating it.

The properties of the silica gel were as follows: SA=346 m²/g, PV=1.96 cm³/g, and Av. Pd=226Å.

As will be seen by comparing the properties of the gel obtained in this Example with the product of Example I, too high a pH and relatively brief heating during the aging step results in a loss of pore volume. The pore volume obtained in Example I was 2.52 cm³/g as compared with only 1.96 cm³/g for Example VI.

EXAMPLE VII

In the runs referred to in the Table below, all the variables during precipitation were maintained as in Example I. After precipitation, the gel was adjusted to a pH of 5.0 by adding H₂SO₄ (1-normal), and was heated to 95°C for 4 hours. Samples were taken at various time intervals during the aging and were washed as in Example 1 before evaluation.

Table I shows the influence of the length of the thermal aging period on the porosity of the gel and on pore distribution.

Table I

	Time (Hrs.)	S.A. (m ² /g)	P.V. (cm ³ /g)	AV. PD (Å)
75	0	757	2.77	147
	1/2	492	2.72	221
	1	394	2.90	294
	1-1/2	355	2.76	311
	2	343	2.77	323
	4	284	2.56	362

- 80 As will be seen from the data reported in Table I the thermal aging of the precipitate should be conducted for a minimum of 1 hour in order to obtain a silica xerogel product having an average pore diameter in the desired range of from 300-600Å.

EXAMPLE VIII

- 85 In this run all the variables during precipitation and heating were maintained the same as in Example I. The gel was then washed as in Example I, but only until the filtrate titrated 100 ppm Na₂SO₄. The product was then treated with acetone and evaluated. The physical properties of the gel were substantially the same as were found for the product of

Example I. However, when the product was calcined in a fluidized bed at about 996°C for 3 hours and evaluated, the properties were as follows: SA=225 m²/g, PV=1.62 cm³/g, Av. Pd=286Å.

As will be seen from the porosity values of the product obtained in this Example when compared to the product of Example I after calcination in a fluidized bed at 983°C, the surface area pore volume and average pore diameter are all adversely affected by the relatively high level of Na₂SO₄ left in the product.

Copending application 39241/69 (Serial No. 1284087) describes and claims the preparation of silica gel in which an organic liquid which forms an azeotrope with water is

- slurry having an SiO_2 concentration of from 5 to 12 wt.%, and a pH of from 3 to 8, the temperature during precipitation being maintained between 0°C and 10°C , b) heating the product of step a) at a pH of from 3 to 8 and at a temperature of from 50 to 100°C for from 1 to 6 hours, and c) washing the product of step b) to remove sodium until the filtrate contains less than 20 ppm by weight of sodium salt, and 2) converting the hydrogel to a xerogel, by d) replacing the water in the hydrogel by a liquid of lower surface tension and e) thereafter drying.
2. A method according to claim 1 wherein the water in the hydrogel is replaced with a water-miscible organic liquid.
3. A method according to claim 2 wherein the water-miscible organic liquid is selected from alcohols, acetone, and mixtures thereof.
4. A method according to any of claims 1 to 3 wherein the precipitation of silica hydrogel in step (a) is accomplished by reducing the pH of the aqueous solution of sodium silicate with an agent selected from acids and ion-exchange resins.
5. A method according to claim 4 wherein 40% of the amount of pH-reducing agent necessary for the precipitation is added over a period of from 30 to 120 minutes and the balance is added during a subsequent period of from 20 to 90 minutes.
6. A method according to claim 5 wherein the first 40% of the pH-reducing agent is added over a period of about 1 hour.
7. A method according to claims 5 or 6 wherein the said balance of the pH-reducing agent is added over a period of about 45 minutes.
8. A method according to any of claims 1 to 7 wherein the SiO_2 concentration in the
11. A method according to any of claims 1 to 10 wherein step (b) is conducted for about 4 hours.
12. A method according to any of claims 1 to 11 wherein step (c) is accomplished by washing with a solution of one or more displacing salts selected from aluminum chloride, aluminum sulfate, ammonium chloride, and ammonium nitrate.
13. A method according to any of claims 1 to 11 wherein step (c) is accomplished by washing with a solution of HCl or H_2SO_4 .
14. A method according to any of claims 1 to 13 wherein step (e) is accomplished by spray drying.
15. A method according to any of claims 1 to 13 wherein step (e) is accomplished by distillation.
16. A method according to any of claims 1 to 15 wherein the precipitated hydrogel is comminuted to a particle size less than 200 microns before or after step (d).
17. A method according to any of claims 1 to 16 wherein the dried xerogel is calcined at a temperature of from 260 to 650°C .
18. A method according to claim 1 for preparing a silica hydrogel substantially as hereinbefore described in Example I, V, or VII.
19. A silica xerogel, which is stable at temperatures up to 1100°C in a fluidized bed and which has a surface of from 200 to $500\text{ m}^2/\text{g}$ the majority of which is provided by pores of a diameter of from 300 to $600\text{\AA}$, prepared by a method according to any of claims 1 to 18.

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