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An emulsion method for producing fine, low density, high surface area silica powder from alkoxides

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Fine silica powders were prepared by the hydrolysis and condensation of an emulsion of tetraethyl orthosilicate (TEOS) droplets in a continuous water phase. No additions of alcohol, as a mutual solvent for the TEOS and water, or of strong acid or base catalysts, as required in the more conventional sol–gel methods, were used. The emulsion was produced by mechanical mixing and was stabilized against separating out of the phases by increasing the viscosity of the water with a commercial thickening agent, Texipol.

The TEOS/water emulsion reacted to form into a loose particulate gel, which could be crushed to a powder after drying at 40 °C. The amorphous silica powders produced had low tapping densities (approximately 0.2 g cm^{-3}), small particle sizes ($<$ 30 nm) and high specific surface areas (50–400 m^2 g^{-1}).

1. Introduction

Oxide powders which are well defined physically and chemically have many industrial applications. They are used for the production of a variety of technical ceramics, glasses and composites with important mechanical, electrical, magnetic or chemical properties. Fine silica powders are used to control the viscosity and thixotropy of liquid systems, as modifying/reinforcing agents to polymer systems, and to alter the caking and flowing properties of other powders. Many other applications exist within the adhesive, pharmaceutical, printing, plastic and agricultural industries. Currently, fumed silica powders are used in the production of thermal insulation materials because of their low densities and high surface areas. Sol–gel processing was examined in this work as a method of producing powders with controlled characteristics which could be matched to those of fumed silica.

In the presence of water, metal alkoxides can be hydrolysed and then polymerized, via condensation reactions, into the oxide of the metal. For example, tetraethyl orthosilicate (TEOS) is hydrolysed according to the following general reaction

$$\mathrm{Si(OR)_4} + x\mathrm{H_2O} \Leftrightarrow \mathrm{(HO)}_x\mathrm{Si(OR)}_{4-x} + x\mathrm{ROH}$$

where R = CH_3CH_2.

The silanol groups formed can then undergo either alcohol or water condensation polymerization with other silanols or with alkoxide groups

$$\equiv\mathrm{Si{-}OH} + \mathrm{R'O{-}Si} \equiv \;\Leftrightarrow\; \equiv\mathrm{Si{-}O{-}Si} \equiv + \mathrm{R'OH}$$

where R′ = CH_3CH_2 or H.

Most of the work carried out previously on producing powders from emulsions has involved the use of water-in-oil type systems. Aqueous metal salt solutions are dispersed in a continuous organic phase (e.g. benzene, toluene or mineral oil) aided by an emulsifying agent. The emulsions are then “dried” to remove the water (or oil in some cases) in order to precipitate the metal oxides as powders. Emulsions can be dried by a range of techniques [1] such as rapid freezing followed by freeze drying, evaporation of aqueous media under vacuum, evaporation by dropping the emulsion into hot kerosene [2] and atomizing the emulsion in a burner.

Different powders have been produced by variations on this basic scheme, for example Al_2O_3 [3, 4], Y_2O_3 [5, 6], $Y(OH)_3$ [7], and $YBa_2Cu_3O_{7-x}$ [8]. One method, based on an emulsion of an aqueous salt solution dispersed in an organic phase, has been used for the production of a wide range of oxide powders [9], including $BaTiO_3$, doped $BaTiO_3$, Nb_2O_5, Al_2O_3, Bi_2O_3, and $YBa_2Cu_3O_x$.

The use of alkoxides in this area has been more limited. Hardy and colleagues [11] have prepared oxide powders from salt solutions and alkoxide

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TABLE I Data showing the reproducibility of tapping density measurements

Powder sample	Powder type	Quoted powder tapping density (g cm^{-3})	Average powder tapping density (g cm^{-3})	Standard deviation of measurements
1	Aerosil 200	0.05	0.051	0.0044
2	Aerosil 300	0.05	0.052	0.0037
3	Aerosil 380	0.05	0.055	0.0065
4	FK320DS	0.08	0.083	0.0041
5	Acid catalysed	–	0.238	0.0022
6	Two-step	–	0.144	0.0024

precursors, using emulsions to control particle size, shape, size distribution and composition. Two methods involved alkoxides. First, they prepared a water-in-oil emulsion with acidified water-droplets in a mineral oil/heptane solution, using surfactants. TEOS was then added via the continuous phase to react with the water droplets to form a powder. This produced less than theoretical density (1.7 g cm^{-3}), high specific surface area (200–400 m^2 g^{-1}) spherical silica particles, approximately a few microns in diameter. The second method involved emulsifying the alkoxide (titanium butoxide, aluminium tri-*sec*-butoxide and zirconium-*n*-propoxide) in acetonitrile. Water was then added to this emulsion to cause hydrolysis and hence powder formation.

Various oxide powders, including $2ZrO_2$–Yb_2O_3 [10], yttria-stabilized zirconia (YSZ) [12], and silica [13] have been produced by using variations of sol–gel-emulsion techniques. In all cases the preparation method significantly affected the droplet size and size distribution and emulsion stability, all of which in turn affected the powder characteristics.

Minehan and Messing [13] reported the production of a whole range of silica particle sizes (0.1 to > 50 μm) from a spontaneous emulsification method, in which an ethanolic solution of partially hydrolysed TEOS was reacted with water; no stirring was necessary but both acid and base catalysts were used.

Some similarities exist between emulsion methods and those employed by Esquivias and Zarzycki in the production of "sonogels". They produced silica gels from the acid catalysis of TEOS, without the use of a solvent [14]. This was achieved by using ultrasound to mix the two components.

In the present work a simple emulsion method for producing fine, low density, high surface area silica powders from alkoxides, is described. TEOS was reacted directly with water, without the use of a solvent such as ethanol and acid or base catalysts, by forming TEOS emulsion droplets in a water continuous phase by mechanical mixing of the two phases. The emulsion was stabilized by increasing the viscosity of the water with a thickening agent, Texipol.

2. Experimental procedure

A simple emulsion system was studied based on the immiscibility of TEOS and water, and consisting of droplets of a dispersed phase of TEOS (98% pure) in a continuous water phase. The emulsions were stabilized by increasing the viscosity of the water in the continuous phase. This was achieved by adding Texipol 63-001, a commercial thickening agent, to the water. The Texipol consists of a copolymer of sodium(polyacrylate) and polyacrylamide dissolved in water and then dispersed as an emulsion in isoparaffin. Small quantities of surfactants are present, but there is no free ammonia in the Texipol.

The Texipol was first dissolved in the water. TEOS was then added and the resulting emulsion was either magnetically stirred or blended for a period of time (usually 10 minutes) and left to react. After gelation of the emulsion it was dried at 40 °C, and lightly crushed to a powder using a pestle and mortar.

After the emulsion had been produced optical microscopy was used to examine the droplet sizes of the TEOS in the water. A few drops of the emulsion were placed in a dimpled glass slide, enclosed with a cover slip and observed in transmitted, non-polarized light.

Powder tapping density measurements were performed using a cylindrical plastic container of known volume, determined by mercury displacement. Before density determination, the powder was dried at 85 °C for approximately 24 h. Powder was added to the container and the container gently tapped by hand to cause the powder to settle. More powder was added as necessary to keep the container full. Tapping was continued until no further settling of the powder was observed. This was usually around 300 taps. The powder was weighed and the tapping density calculated. The standard procedure was to take an average of three readings. The accuracy of the method was tested by comparing the measured tapping densities of commercially available powders (Aerosil and FK320DS, both produced by Degussa) to those quoted by the manufacturer and good agreement was found (Table I).

Measurements were also carried out for two different sol–gel derived powders, and the standard deviations obtained are given in Table I. The powders in Table I were produced by non-emulsion methods in which silica particles were precipitated from a solution of TEOS and water in alcohol. The reaction of the TEOS can be catalysed by either a single addition of acid (hydrochloric acid for sample 5) or by two separate additions of catalysts (the two-step method referred to in Table I used additions of HCl followed by ammonia solution). Further details of these methods and the powders in Table I have been reported elsewhere [15, 16].

The tapping densities were reproducible, this reproducibility being slightly reduced by taking the average of only three measurements and by any crushing of the powder that occurred. The reproducibility decreased as the tapping density was reduced. Overall, when all these factors were taken into consideration, the reproducibility of the powder tapping density method was determined to be better than ± 5%.

The powders were examined by transmission electron microscopy (TEM) using a Philips EM400T operating at 100 kV. Powders were prepared for examination by ultrasonically dispersing a small quantity in methanol. A few drops of this solution were then placed onto a 300 mesh copper grid covered with a carbon film. The drying of the grids was assisted by placing them on a filter paper. The primary particle sizes in the powders were determined by measuring approximately 30–50 particles from randomly taken TEM micrographs. The primary particle size range was defined as that including approximately 90% of the particles measured.

Specific surface areas were measured by gas adsorption [15] using the Brunauer, Emmet, and Teller (BET) method [17]. The time to phase separation of the TEOS/water emulsion was observed visually and was defined as the moment at which one of the emulsion components formed an immiscible layer distinct from the emulsion.

The reaction yield of silica powder was calculated as the actual weight of powder produced, as a percentage of the maximum theoretical quantity possible based on the amount of TEOS used. It is possible for the apparent yield to be greater than 100% because of retained organics and water in the powder which increase its weight.

3. Results

It was possible to react TEOS and water without the use of a solvent by continuous fast magnetic stirring and this would result in gelation. However, the emulsion was very unstable and completely separated into two layers in about 15 s if magnetic stirring ceased, and once the emulsion separated into two layers no gelation occurred.

To increase the stability of the emulsions a commercial thickening agent, Texipol, was used to raise the viscosity of the water. Texipol did not mix with pure TEOS, but was soluble in water which it thickened effectively. By these means it was possible to form TEOS-in-water emulsions which were stable against phase separation for greater than six days. The water, once thickened with Texipol, remained as a stable solution before the TEOS was added. A solution of water with 0.4 vol % of Texipol remained apparently unchanged for one month.

The compositions and characteristics of the emulsions and powders produced are given in Table II.

Depending on the relative quantities of the reactants, all the emulsions gelled after a period of a few days to two weeks (except for sample E2). In some

TABLE II Concentrations of emulsions and characteristics of the powders produced

Sample	Composition (% by volume)			Approx. droplet size range (μm)	Primary particle size range (nm)	Powder tapping density (g cm^{-3})	Silica yield (% of maximum)	Time to phase separation	Specific surface area (m^2 g^{-1})	Product	Time to gel (days)
	Texipol	Water	TEOS								
E1	0.2	96.8	3	4–44	–	–	62	> 6 days	–	[a]	7
E2	0.03	82.97	17	44–222	–	–	–	0.5 h	–	No gelation	–
E3	0.2	82.8	17	22–67	8–24	0.17	91	24 h	256	Op. friable gel	5
E4	1.1	81.9	17	4–44	12–24	0.21	26	> 6 days	–	[a]	7
E5	0.2	69.8	30	–	–	0.15	103	Continuously stirred	392	Op. friable gel	4
E6	0.2	70.8	29	44–176	10–24	0.17	99	24 h	–	Op. friable gel	3
E7	0.4	71	28.6	–	–	0.19	42	No separation	72	Op. friable gel	2.5
E8	0.6	71	28.4	–	–	0.16	55	No separation	65	Op. friable gel	8–10

[a] Gelation occurred on the edge of the reaction container.

Op. = Opaque.

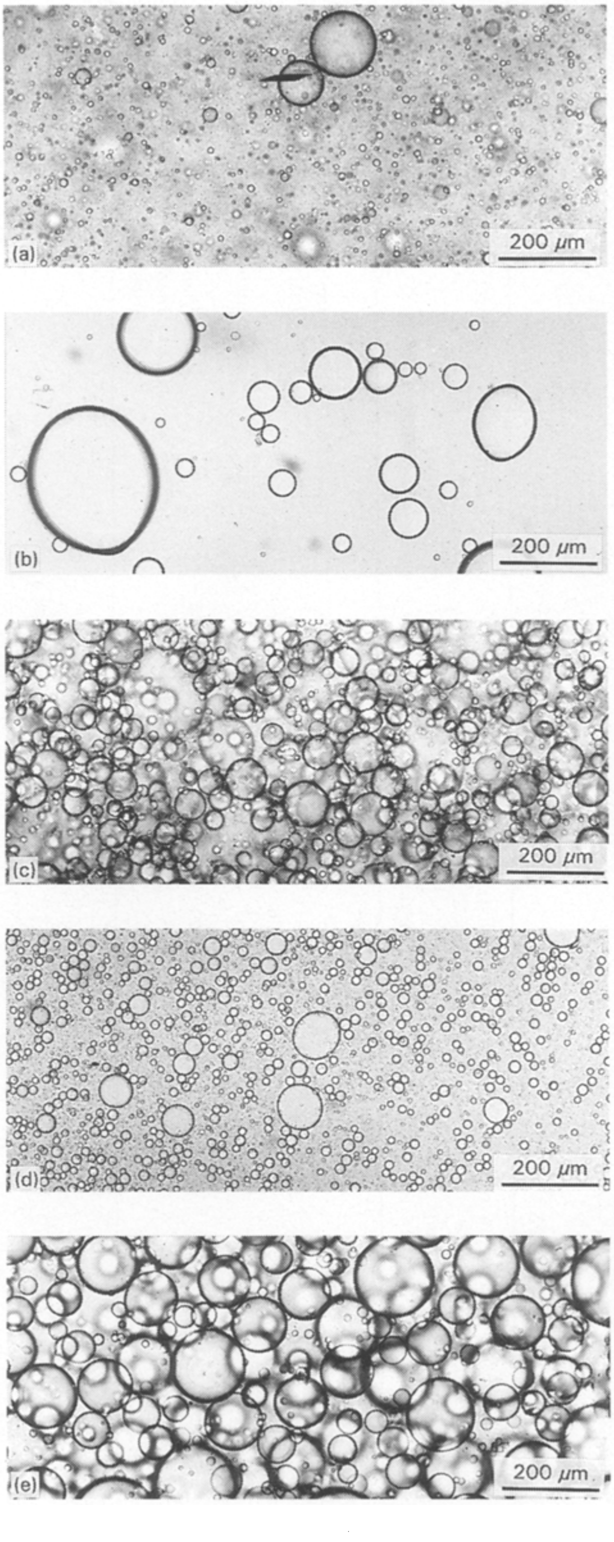

Figure 1 Optical micrographs showing the TEOS droplets in a continuous phase of water in the concentrations shown in Table II: (a) sample E1, (b) sample E2, (c) sample E3, (d) sample E4 and (e) sample E6 (bars = 200 μm).

cases, before the emulsion gelled the larger TEOS-rich droplets floated to the surface leaving two distinct layers, both of which gelled. Optical microscopy showed that, before gelation, the bottom layer contained a lower volume of TEOS rich droplets and these had a smaller average diameter.

After drying the gels were opaque, powdery solids which were mechanically weak and friable. These gels easily yielded fine, low density powders by gently grinding.

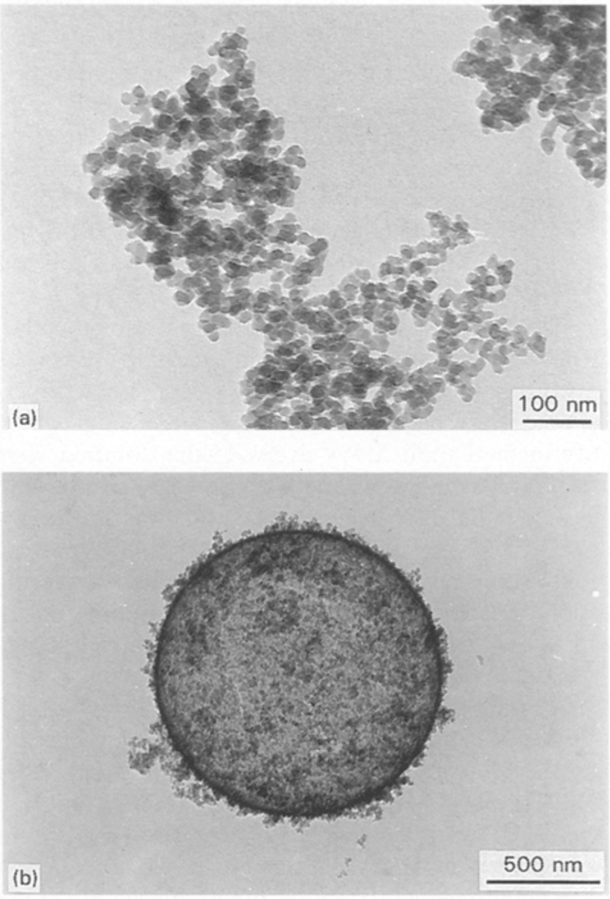

Figure 2 TEM micrographs of the powder produced using the TEOS-in-water emulsion method, sample E3: (a) bar = 100 nm and (b) bar = 500 nm.

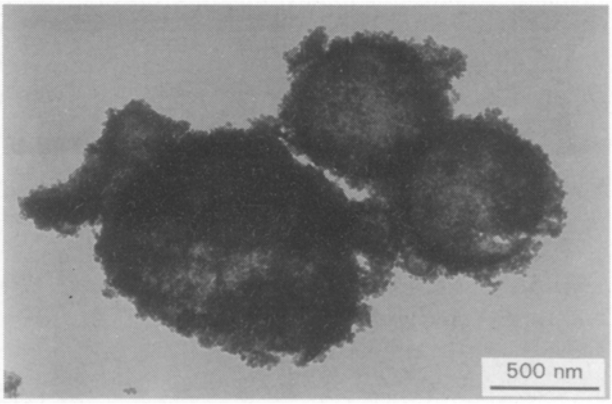

Figure 3 TEM micrograph showing the variation in the size of the ‘dried emulsion droplet’ type features (sample E4): bar = 500 nm.

The droplet sizes (Table II) were obtained from optical micrographs taken of the solutions immediately after stirring stopped (Fig. 1). The droplets visible in the micrographs were demonstrated to be TEOS and not just air, as a solution of water and Texipol gave no visible droplets.

Powder sample E3 had a specific surface area of 256 $m^2 g^{-1}$. TEM micrographs are shown in Fig. 2. The powder consisted mainly of well defined but agglomerated primary particles (Fig. 2(a)). TEM of the powders produced from emulsions E4, and E6 showed primary particle sizes and structures similar to those in Fig. 2(a). Fig. 2(b) clearly depicts agglomerated particles formed within an emulsion droplet.

A wide range of sizes of these structures arising from emulsion droplets were observed in TEM micrographs (Fig. 3).

The stability of the emulsions towards phase separation was increased by raising the Texipol concentration. Samples E8 and E7 (Table II) gelled to opaque friable gels before any visible phase separation occurred. Sample E4 did not separate before gelation also, although in this case the gelation occurred on the edges of the reaction container and did not involve all of the liquid present; hence the lower yield obtained when compared to sample E3. In general, the powder yields were lower for the higher viscosity emulsions, i.e. those containing more Texipol. Higher Texipol concentrations were also associated with longer gelation times.

The tapping densities showed no significant variation with Texipol concentration. Again TEM showed samples E8 and E7 to have similar particle structures and sizes to those in Fig. 2(a).

The pH of the TEOS/water/Texipol emulsions ranged from 5.0–6.5 depending on the actual concentrations of the components.

To stop phase separation at low Texipol concentrations, emulsion E5 was stirred continuously until gelation. It gelled in four days and after drying crushed to a powder with an equivalent yield and a slightly lower density than the same composition not stirred continuously (E6).

4. Discussion

TEOS and water are immiscible and an emulsion was produced with TEOS as the dispersed phase and the water as the continuous phase. The purpose of using an emulsion technique was twofold; to attempt to limit or control particle size, or aggregate particle size, using the emulsion droplet size and to investigate the effects on the powder characteristics compared to other processing techniques.

The first TEOS-in-water emulsions produced were unstable and completely separated in about 15 s if magnetic stirring ceased. Stable emulsions were produced by increasing the viscosity of the water phase using a commercial thickening agent (Texipol). This stabilized the emulsions by increasing the viscosity of the water which slowed the droplet coalescence and phase separation.

It was found that even without the addition of catalyst, most of the emulsions gelled and then dried to a friable, easily crushed opaque gel. In general, the emulsions produced low tapping density powders with fine primary particle sizes. Some emulsions used in this work gave low silica yields. For example, the yield from emulsion E4 was 26% which indicates that a considerable amount of TEOS must have remained unreacted. The yields of silica powder produced by this method were generally lower than by the single step [18] and two-step [19] sol–gel methods used to produce similar low density powders from more concentrated alkoxide sol–gel routes, but could approach 100% in some cases, e.g. E3, E5, and E6.

Optical micrographs (Fig. 1) of the stable emulsions produced from the compositions given in Table II show that an increase in the Texipol concentration, or a decrease in the TEOS concentration tends to give a smaller droplet size in the emulsion because of the increased emulsion stability. A low Texipol concentration (sample E2) results in the emulsion being insufficiently stable for the purpose of this experiment. Too large a concentration of Texipol, although it makes the emulsion more stable, tends to reduce the efficiency of the reaction, as illustrated by the low yield for samples E4, E7, and E8.

Decreasing the TEOS concentration (sample E1) increases the emulsion stability, but a large volume of solution is obviously necessary to produce a realistic amount of powder. It is possible to increase the TEOS concentration (sample E6) without detriment to the properties of either the emulsion or the powder produced.

The powders produced were similar to those produced by the two-step sol–gel method [19], with low tapping densities, small primary particle sizes (Table II) and open agglomerate structures (Fig. 2(a)). The emulsion powders also had a much narrower primary particle size range than the equivalent low density powders produced by the two-step method. Fig. 2(b) clearly shows particles formed within an emulsion droplet. It is likely that this has formed from an emulsion droplet as similar structures have been observed in all TEM micrographs of powders produced by the emulsion method. Lack of large numbers of such droplet-like agglomerate structures in the TEM, could be caused by the break up of the larger TEOS droplets during the reaction with water. The hydrolysis of TEOS molecules at the droplet surfaces releases ethanol (four moles for each mole of TEOS). The increased solubility of the water phase with the TEOS arising from both the production of ethanol and the formation of partially hydrolysed TEOS molecules (which are more water soluble) would lead to dissolution of TEOS droplets and a tendency for disappearance of the emulsion. The emulsions do not, however, appear to deteriorate completely before the production of silica particles, as shown by the presence of some spherical particle agglomerates.

In the compositions examined (Table II) a catalyst was not necessary. Without a catalyst the hydrolysis and condensation of TEOS is normally extremely slow, but these TEOS-in-water emulsions gelled reasonably fast (over a period of days) without a catalyst. This may be caused by several factors. The addition of Texipol changes the pH of the solutions to between 5 and 7, from just below 7. In this range the hydrolysis rate of TEOS is slow, but the condensation rate is high [20]. It is possible that this change is significant enough to catalyse the reaction. However, it is also possible some constituent of the Texipol catalysed the reactions, although this seems unlikely given the constituents of Texipol.

An alternative explanation of the reasonably fast reaction speed could be the large interfacial area between TEOS droplets and the water available for reactions. Also, the effects of being at the surface of a droplet may render the TEOS molecule more susceptible to hydrolysis by, for example, altering its stability. Both the interfacial area and pH effects may be expected to contribute to the gelation observed.

Some of the emulsions produced a very low powder yield (< 50%). This is indicative of unreacted TEOS, which would evaporate when the powder was dried. The lower yields were associated with higher Texipol concentrations and longer gelation times.

The emulsion method described is significant because of the useful characteristics of the powders produced and has the following advantages:

(a) Emulsions which have been used previously for powder production have generally involved dispersion of an aqueous salt solution in an organic continuous phase. The only example of an alkoxide as the dispersed phase used acetonitrile as the continuous phase to disperse titanium, aluminium and zirconium alkoxides [11]. Therefore, the present system is simple and safe.

(b) The emulsions described in the present work can be simply oven-dried and no complex drying procedures are necessary to recover the powder from the emulsion. Often complex drying and recovery procedures are necessary [1, 2].

(c) Ethanol is not required as a solvent for the TEOS and water, although it is generally used in relatively large quantities in the conventional sol–gel route applied to TEOS. The present system is simpler and water is also preferable to ethanol for the bulk of the solution from an economic point of view.

(d) In the conventional sol–gel route an acid or base catalyst, such as HCl or ammonia, is required for the reaction to proceed at a reasonable rate. Even when producing sonogels a catalyst has been used [14]. In the present work no strong acid or base catalyst was used, although it is possible that the Texipol may be acting as a weak acid catalyst.

5. Conclusions

Stable emulsions of TEOS-rich droplets in a continuous phase of water were formed if the viscosity of the water was increased by the addition of a thickening agent, Texipol. The size of the TEOS droplets tended to decrease on increasing the Texipol concentration or reducing the TEOS concentration. Under these conditions the emulsion gelled and when dried produced a silica powder with a low tapping density, high specific surface area, and small primary particle size.

The emulsion method described has a number of important advantages over the more common aqueous salt solution emulsion methods and the traditional alkoxide/ alcohol/water/catalyst sol–gel methods. The present system is simpler and safer than common emulsion methods that require an organic continuous phase; the powders produced from this method can be conveniently recovered from the emulsions by drying at low temperature in an oven; no ethanol is required as a solvent for the TEOS and water, and no additional strong acid or a base catalyst is required to give a rapid reaction rate.

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