Polymer Bulletin 24, 173–179 (1990)

Polymer Bulletin

A novel technique for preparing organophilic silica by water-in-oil microemulsions

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Summary

A novel technique to prepare ultramicro spherical silica particles containing vinyl groups on their surfaces is presented. This process is a combination of the sol-gel technique and the water-in-oil microemulsion technique in which hydrolysis and condensation of TEOS [$Si(OEt)_4$] and MPS (trimethoxysilylpropylmethacrylate) take place. Spherical silica particles with a size range from 20 to 70 nm were obtained and the surface concentrations of the double bonds per nm^2 were from 4 to 7.

Key words: sol-gel, silica, water-in-oil emulsion, microemulsion.

Introduction

Until recently few works dealt with the possibility of producing oxide powders by microemulsion systems (1-5). Among these studies, different water-in-oil (w/o) microemulsions, using different oil/surfactant systems were employed (1-5).

In our study, a new way of producing ultramicro spherical organophilic silica particles, i.e., silica containing alkyl groups on its surface is described. The basic idea of this procedure consists of the introduction of an organic functional group R on the silica surface by means of co-hydrolysis and co-condensation between tetraethoxysilane and trialkoxy-organosilane as starting materials.

Usually, organophilic silica or modified surface silica particles are obtained by surface modification of silica (10-18). One of these techniques is the one which has been developed by Vrij et al. (18) which consists of the esterification of hydrophilic silica obtained according to the Stöber process (17). This approach requires a lot of precautions to avoid irreversible aggregation of the particles, and this necessitates keeping the water content as low as possible just before the esterification reaction. In addition the purification of the esterified silica is a very critical step considering that a succession of centrifugation and redispersion with ultrasound must be made. In these cases, it is usually difficult to obtain individual particles. Nonetheless, powdered silica such as the Aerosils from Degussa can be used but in that technique, agglomerates are always present.

In our case, individual organophilic silica particles with a narrow size distribution are obtained. In addition, the formation of the silica particles and their hydrophobisation are carried out in one step, in one reaction vessel and at room temperature. This new way of producing organophilic silica particles is the result of the combination of the sol-gel process and water-in-oil (w/o) microemulsion technique, where both TEOS and organotrialkoxysilane are mixed. The size of the water droplets in the emulsion is one of the determining factors of the final silica particle size.

In this study, trimethoxysilylpropyl methacrylate (MPS) is used as the organotrialkoxysilane so as to obtain silica particles containing vinyl groups on their surfaces.

These vinyl groups could be useful for a number of applications, including bonding of the particles into a surrounding elastomeric matrix.

Experimental

Materials. Aerosil OT or "AOT" (sodium bis-2-ethylhexylsulfosuccinate) was purchased from the American Tokyo Kasei Co. and polyoxyethylene (4) lauryl ether (POELE) from Aldrich.

Tetraethoxysilane (TEOS) and trimethoxysilylpropyl methacrylate (MPS) were respectively supplied by Petrarch Systems Inc. and the Aldrich Chemical Company. A 29% ammonia solution as well as toluene and cyclohexane were obtained from Fisher Scientific Inc..

All components were used without further purification. The water was deionised.

Procedure. Water-in-oil microemulsions were prepared by adding ammonia and water to a solution of surfactant [AOT or polyoxyethylene (4) lauryl ether] in an organic solvent (respectively toluene or cyclohexane). Then TEOS and MPS were added into the erlenmeyer flask containing the w/o emulsion. The reaction took place at room temperature and the emulsion was stirred for 3 days. In tests #1 to 7 a mixture of TEOS and MPS was used, whereas in test #8 TEOS was added first and MPS in a second step 24 hours later. All the other reaction conditions were kept constant. The initial amount of solvent was 50 g and the molar amounts of TEOS and MPS were 4.5×10^{-3} and 3.5×10^{-3}, respectively. Ammonia was chosen as catalyst.

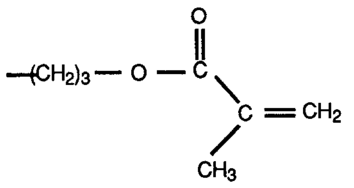
Reaction Scheme. This procedure, termed bulk modification, consists of a co-hydrolysis and co-condensation of TEOS and MPS in the microemulsion system. Basically, the reaction can be viewed as a 2-step process, as shown below:

Hydrolysis

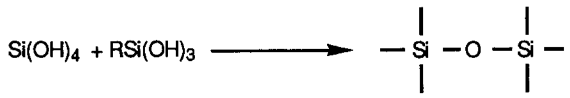
$$Si(OEt)_4 + 4\,H_2O \longrightarrow Si(OH)_4 + 4\,EtOH \qquad (1)$$

$$R\,Si(OMe)_3 + 3\,H_2O \longrightarrow RSi(OH)_3 + 3\,MeOH \qquad (2)$$

where R is



Condensation



$$Si(OH)_4 + RSi(OH)_3 \longrightarrow -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-$$

Both TEOS and MPS undergo hydrolysis with the emulsified water to generate silanol groups. These can then condense to form Si-O-Si linkages. However, hydrolysis and condensation can, and most likely do, take place simultaneously.

Characterization methods. Colloidal silica particles were centrifuged out at 15,000 rpm and the resulting precipitate washed with toluene, and with a mixture of water and toluene in order to remove the emulsifier.

After this washing process the silica was dried under vacuum at 70°C for 6 hours, and IR spectra were obtained using a Perkin Elmer 1600 FTIR Spectrometer.

Density measurements of these dried silica samples were carried out using a tube graduated every 0.01 ml. The density was determined by measuring the deplacement volume of water contained in the tube by adding a known amount of the silica powder.

Elemental analyses for Si and C were performed by Galbraith Laboratories Inc.

Transmission electron microscope measurements were performed with a Hitachi apparatus. Carrier copper grids covered with carbon-coated film were dipped in the dilute silica dispersions.

Determination of vinyl content was performed by iodometric titration.

Results and Discussion

General characterization. All the samples studied are listed in Table I. As already mentioned, in test #1 through 7 a mixture of TEOS and MPS was directly added to the emulsion, whereas in test #8 MPS was added 24 hours after the addition of TEOS.

The experimental results illustrating the effect of water, emulsifier and ammonia content are first discussed. Then some related interpretations are offered. The reaction conditions for tests #1 through 8 are given in Table I. The amount of the different chemicals used in this process are chosen according to different criteria: A minimum amount of water is required in order to realize this process.

1) a stoichiometric amount to hydrolyze the alkoxides (TEOS + MPS)
2) a minimum amount to keep a stabilized emulsion, depending on the phase diagram of the w/o system.

Table I Composition of Samples

Test #	Solvent	Water	Emulsifier	TEOS	MPS	Ammonia
1	cyclohexane	2.5 g 0.138 mole	POELE 9g 0.0249 moles	0.95 g 0.0045 mole	0.86 g 0.0035 mole	0.45 g
2	Toluene	2.5 g 0.138 mole	AOT 10 g 0.0225 mole	0.95 g 0.0045 mole	0.86 g 0.0035 mole	0.45 g
3	Toluene	1.62 g 0.09 mole	AOT 10 g 0.0225 mole	0.95 g 0.0045 mole	0.86 g 0.0035 mole	0.45 g
4	Toluene	0.4 g 0.0225 mole	AOT 10 g 0.0225 mole	0.95 g 0.0045 mole	0.86 g 0.0035 mole	0.45 g
5	Toluene	2.5 g 0.138 mole	AOT 13 g 0.030 mole	0.95 g 0.0045 mole	0.86 g 0.0035 mole	0.45 g
6	Toluene	2.5 g 0.138 mole	AOT 10 g 0.0225 mole	0.95 g 0.0045 mole	0.86 g 0.0035 mole	0.30 g
7	Toluene	2.5 g 0.138 mole	AOT 10 g 0.0225 mole	0.95 g 0.0045 mole	0.86 g 0.0035 mole	0.60 g
8	Toluene	1.62 g 0.09 mole	AOT 10 g 0.0225 mole	0.95 g 0.0045 mole	0.86 g 0.0035 mole	0.45 g

Concerning this latter type of water, two kinds have to be considered:

- the solvation water, which is strongly bonded to the hydrophilic head group of the surfactant.
- the bulk water, pooled into the core of the micelle, which is more mobile.

Thus, it is assumed that the bulk water will be very reactive in the hydrolysis reaction compared with the less reactive water bonded to the hydrophilic head group inside the reverse micelles. It seems then obvious that the water/surfactant ratio n and the water/alkoxide ratio h will be important parameters governing the hydrolysis reaction. According to the schematic phase diagram of the system AOT/toluene/water determined by F. Candau (6), all the experiments were carried out in the microemulsion domain. Transmission electron microscopy of tests # 1 through 8 confirms that small spherical and individual particles can be obtained using this process (Figure 1). The particle size as a function of the reaction conditions is described in Table 2, where Dp is the average particle diameter and σ_{n-1} is the standard deviation.

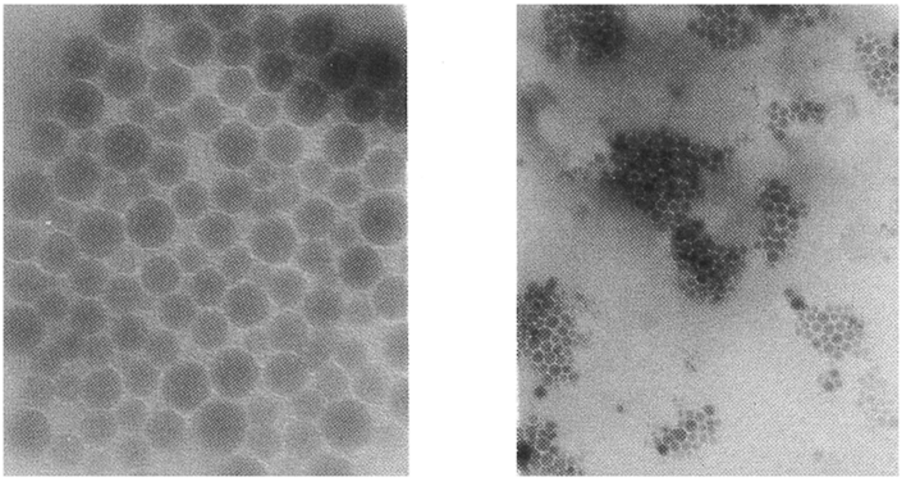


Figure1. Transmission electron microscopy of: a) sample #2 b) sample #5.

Table 2 Reaction Conditions and Average Particle Diameters

Test #	molar ratio n Water/surfactant	molar ratio hx Water/alkoxides	water stoichio- metric excess/mole	Dp/nm	σ_{n-1}
1	5.5	17	4.9	28	3.2
2	6	17	4.9	65	14.5
3	4	11	3.1	25	4.0
4	1	2.8	0	20	4.0
5	4.6	17	4.9	33	4.5
6	6	17	4.9	42	9.7
7	6	17	4.9	64	21
8	4	11	3.1	23	4.0

It appears that when decreasing the amount of water (tests #2 and 3), or when increasing the amount of emulsifier tests (#2 and 4), the particle size decreases. This result indicates that the water droplet sizes is one of the determining factors of the particle size, as expected.

The silica density was measured as described previously with samples #1-4, and was found to be the same value, 1.7 g cm^{-3}, for all of them.

Infra-red spectroscopy (Figure 2) indicated the presence of the double bonds of the MPS, (1637 cm^{-1}), the Si-O-Si linkage 1100 cm^{-1}, the carbonyl group 1715 cm^{-1}, ν (CH_2) = 2737 cm^{-1}, ν (CH_3) = 2940 cm^{-1}. No peaks belonging to the emulsifier can be observed. Condensation between MPS and TEOS is confirmed.

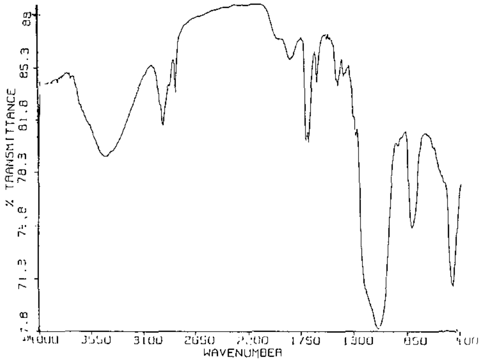


Figure 2. infra-red spectroscopy of one silica sample(sample #2).

Elemental analysis of samples #2 and 3 were performed. These results, shown in Table 3, confirm condensation between TEOS and MPS.

Table 3 Results of Analytical Analyses

Test #	% C Measured	% Si Measured
2	32.7	18.5
3	35.9	14.2

From test #1 we can see that the choice of the system emulsifier/solvent/water is of great importance. Each system leads to different results (test #1-7), and thus need to be studied separately. This result is interesting because it shows that it is possible to choose the microemulsion system so as to produce organophilic silica, consistent with the desired applications.

Surface characterization. The double bond content on the silica surface was determined by iodometric titration, which gives the iodine number (7). The iodine number is the number of grams of iodine absorbed by 100 g of sample (here silica) under standard conditions.

In a typical test, 5 ml of Wiijs solution is added to 20 ml of silica emulsion. The flask is then sealed and kept in the dark for 24 hours. At this stage 20 ml of KI solution is added. The mixture is then titrated with a solution of $Na_2S_2O_3$. Specifically, $Na_2S_2O_3$ is added until the emulsion color changes from brown to white. Then soluble starch is added as indicator. If the color darkens, more $Na_2S_2O_3$ is added until the solution becomes clear. The purpose of this titration is to measure the iodine content which comes from the ICl which did not react with the vinyl groups, and has thus been converted into I_2. This iodine is quantitatively reduced to iodide by titration with $Na_2S_2O_3$. The method requires use of a blank, which consists of an emulsion containing the same amounts of toluene, ammonia, emulsifier, TEOS, and water as the studied samples in which MPS has been replaced by TEOS. In that case the blank does not contain any vinyl groups. This titration allows us to determine the accessible double bonds. The number of silica particles per liter of emulsion can be determined by the formulas $m_s = N_p\ m_p$ where m_p is the weight of 1 particle /g, N_p is the # of particles /l,m_s is the silica weight in g/l,and $m_p = \rho\ Vp = \rho\ (\pi/6)\ D_p^3$ where ρ is the silica density g cm^{-3}, D_p is particle diameter in cm, and thus therein $N_p = 6\ m_s/\pi\ D_p^3\rho$.

According to Tables 4 and 5 and tests #2-5, the bigger the silica particle, the larger the number of double bonds on the surface, and the larger the number per unit area, as expected.

Table 4 Volume Concentrations of Vinyl Groups

Test #	iodine #	# of vinyl groups /g of silica x 10^{-20}	# of vinyl groups /l of emulsion x 10^{-22}
2	18	4.12	1.19
3	26	6.17	1.60
5	26	6.17	1.45
8	31	7.40	1.89

Table 5 Surface Concentrations of Vinyl Groups

Test #	$D_p$nm	N_p/l of emulsion x 10^{-18}	# of vinyl groups/particle	# of vinyl groups/nm^2
2	65	0.118	101,000	7.6
3	25	1.86	8,600	4.4
5	33	0.756	19,800	5.8
8	23	2.36	8,010	4.8

However, adding MPS later in the emulsion (test #8) does not improve considerably the double bond concentration on the surface. This result gives important information on the formation of particles. It indicates that the condensation of $Si(OH)_4$ is faster than the condensation of $RSi(OH)_3$, for the R employed. This result is in agreement with other studies (19-20).

According to the vinyl concentration per nm^2, it seems that for each particle size, the maximum coverage is obtained. These figures are in agreement with the hydroxyl coverage of most hydrophilic types of silica (16).

Conclusions

This new way of producing hydrophobic silica is an important advance. It is interesting because it allows one to obtain hydrophobic silica with a size range from 20 to 70 nm with a narrow size distribution in a simple manner: these particles are obtained by a one-step process, at room temperature.

Acknowledgement

It is a pleasure to acknowledge the financial support provided by Rhône-Poulenc.

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Accepted May 15, 1990 K