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ORIGINAL CONTRIBUTION

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Hydrocarbon dispersion of nanospherical silica by a sol–gel process.
1. Tetraethoxysilane homopolymerization

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Abstract This study focused on the preparation of a hydrocarbon dispersion of nanospherical silica using tetraethoxysilane homopolymerization by a sol–gel process catalyzed by NH_4OH in ethanol. The silica surface was rendered hydrophobic by the introduction of trimethylchlorosilane or trimethylethoxysilane as a terminator. Organophilic particles with diameters in the range 10–130 nm were obtained under controlled conditions. Nevertheless, the organophilic fraction dispersed in hexane was not greater than 62%. The homopolymerization reaction time was directly related to the particle size and, in some cases, its insolubility. High terminator concentration and low termination temperature favored the increase in the number of organophilic particles. The chlorine-containing terminator was more efficient in promoting the production of hydrocarbon hydrophobic nanospheres.

Key words Nanospheres · Sol–gel process · Colloidal dispersion · Tetraethoxysilane

Introduction

Organic microgels with reactive groups have been obtained mainly by emulsion polymerization. This technique does not allow the preparation of organic–inorganic spherical hybrid materials [1]; however, they have been prepared by a sol–gel process [2–4]. The hybridization of polymeric organic and inorganic polymers has been accomplished with the objective of obtaining materials with high performance, such as more thermally resistant silicon-based hybrid materials. In this context, nanospheres with a size in the range of nanometers constitute a class of materials that have special properties due to their sizes [1, 5].

Several routes of microsphere preparation by a sol–gel process have been described in the literature, especially for ceramic and metallic materials application [5, 6–11].

Particles of macromolecular dimensions obtained from the sol–gel process have been receiving great attention. They are generally formed by the polymerization of inorganic monomers frequently derived from organometallic precursors in solution [1, 5, 6]. In these processes, the polymeric chains grow until they reach a critical molecular weight where the macromolecule becomes unstable in solution and is insoluble [12, 13].

The sol–gel process is essentially a physical chemistry route that allows one to obtain high-purity inorganic materials, with a wide variety of forms, such as powders, fibers and films [6]. It is known that sol–gel type reactions with tetraethoxysilane (TEOS) result in linear polymers when the reaction is catalyzed by acids or in microspherical polymers in the presence of basic catalysts [7, 14]. The sol–gel reaction of TEOS, methyltriethoxysilane or dimethyldiethoxysilane systems in alcoholic solution and catalyzed by alkalis have been used for the preparation of silica–silicon hybrid nanospheres [15]. Depending on the synthesis conditions they are hydrophobic (organophilic) particles dispersible in organic solvents [1, 5, 6].

The present work reports the use of only one monomer, TEOS, for the synthesis of polymeric nanospherical silica dispersible in aliphatic hydrocarbons. Dispersion was achieved with the introduction of a terminator into the reaction system at the end of the homopolymerization process. The terminator controls the size of the particle and the modifies the polarity of its surface. The main aim of this work was the preparation of microspherical organophilic silica particles with a size in the range 10–100 nm that were dispersible in hydrocarbons. These microspherical silica particles will be used as a metallocene support.

Experimental

Materials

TEOS, NH_4OH 28% aqueous solution, ethanol, *n*-hexane, trimethylchlorosilane (TMCS), trimethylethoxysilane (TMES) and potassium bromide were supplied by Wako Pure Chemical, Japan, and were used as received. Commercial Aerosil was supplied by Aerosil Nippon.

Nanosphere preparation

The synthesis of the silica nanospheres by the sol–gel reaction using TEOS as the monomer was accomplished using the following procedure.

The reaction was carried out in a 100-, 250- or 500-ml glass reactor at atmospheric pressure. The monomer (TEOS), the solvent (ethanol) and a prescribed amount of catalyst (NH_4OH) were introduced and the reactor was placed in a liquid bath at 50 °C under magnetic stirring. The reaction time varied for each reaction (Tables 1, 2, 3, 4). After the reaction, a hexane solution of the terminator (TMCS) was added to the system and the heating bath was removed when a lower terminator temperature was used. The resulting reaction mixture remained under stirring for 16 h at the desired temperature. After this time period, the solution contained two phases: one rich in ethanol and the other rich in *n*-hexane (the terminator solvent). The two phases were separated and solid residues were obtained by vacuum drying at 40 °C. The solid residue from the ethanol phase containing the insoluble silica and the salt formed in the reaction was washed with water to recover the hexane-insoluble microspheres. The solid powder of organophilic nanospheres was also recovered by vacuum distillation of the hexane and was kept under a controlled atmosphere until it was analyzed by light scattering and Fourier transform (FT) IR spectroscopy [10, 16].

Table 1 Effect of the reaction time of the growth step on the structure of the nanospheres. Tetraethoxysilane (*TEOS*) concentration: 0.6 mol/l; reaction solvent: ethanol; temperature: 50 °C; number-average particle diameter: D_n; r = 8.4 mol H_2O/mol Si; NH_4OH concentration: 0.1 mol/l; particle size dispersion index: D_w/D_n

Sample number	$(CH_3)_3SiCl$ (mol/l)[a]	Reaction time (h)	Organophilic nanospheres (%)[b]	D_n (nm)	D_w/D_n
5/16	0.23	0.33	23.6	10.7	1.04
5/18		0.67	9.4	52.8	1.07
5/20		1	14.1	124.1	1.32
7/32	0.67	2	56.3	14.5	1.03
7/33		4	61.5	10.7	1.03
7/34		6	19.4	13.4	1.10
7/35		24	48.6	126.7	1.29

[a] Terminator concentration (trimethylchlorosilane)
[b] Dispersed in hexane

Characterization of the hydrophobic nanospheres

Light scattering analysis was made using Otsuka DL: S-7000T equipment. This technique determined the size of the particles. Ethanol, the solvent in which the nanospheres were also dispersed, was used as the medium for the analysis.

The IR spectra of the nanospheres were recorded using a Shimadzu model 4200 FTIR spectrometer. The spectra were obtained at a resolution of 2 cm^{-1}, with 20 scans. The samples were examined as KBr disks. The presence of characteristic IR bands of individual groups allowed the identification of the

Table 2 Effect of the terminator concentration on the dispersion of the nanospheres. Reaction time (growth step): 4 h; reaction solvent: ethanol; temperature: 50 °C; termination step of 16 h; TEOS concentration: 0.6 mol/l; r = 8.4 mol H_2O/mol Si; NH_4OH concentration: 0.1 mol/l

Sample number	NH_4OH (mol/l)[a]	$(CH_3)_3SiCl$ (mol/l)[b]	Organophilic nanospheres (%)[c]	D_n (nm)	D_w/D_n
2/6	0.97	0.04	3.0	29.1	1.04
2/7	1.95	0.07	4.4	–	–
2/8	3.89	0.14	7.5	–	–
7/33	–	0.67	61.5	10.7	1.03

[a] Termination step
[b] Terminator concentration
[c] Dispersed in hexane

Table 3 Terminator efficiency in the TEOS homopolymerization. TEOS concentration: 0.6 mol/l; r = 8.4 mol H_2O/mol Si; initial NH_4OH concentration: 0.1 mol/l; solvent: ethanol; terminator: *A* = trimethylchlorosilane and *B* = trimethylethoxysilane; terminator concentration: 0.23 mol/l; reaction temperature: 50 °C; termination NH_4OH concentration: 34.2 mol/l

Sample number	Reaction time (min)	Terminator	Organophilic nanospheres (%)[a]	D_n (nm)	D_w/D_n
5/16	20	A	14.0	10.7	1.04
5/17		B	6.5	–	–
5/18	40	A	24.0	52.8	1.07
5/19		B	14.9	28.7	1.39
5/20	60	A	15.0	124.1	1.32
5/21		B	8.4	–	–

[a] Dispersed in hexane

Table 4 Organophilic silica nanospheres prepared by a sol–gel process using different reaction times and termination temperatures. TEOS concentration: 0.6 mol/l; r = 8.4 mol H_2O/mol Si; initial NH_4OH concentration: 0.1 mol/l; solvent: ethanol; terminator: trimethylethoxysilane; Terminator concentration: 0.235 mol/l; reaction temperature: 50 °C

Sample number	Reaction time (min)	Termination temperature (°C)	Termination time (h)	Organophilic nanospheres (%)[a]	D_n (nm)	D_w/D_n	NH_4OH termination (mol/l)
5/17	20	Room temperature	16	6.5	–	–	34.2
5/19	40			14.9	28.7	1.39	
6/23	20	50	4	0.02	–	–	39.7
6/24			24	0.15	35.4	1.08	
6/25	40		4	0.02	–	–	
6/26			8	0.03	–	–	
6/27			24	0.43	73.4	1.33	
6/28	30		24	0.22	–	–	
6/29			48	0.61	–	–	
6/30			4	0.07	–	–	69.3

[a] Dispersed in hexane

molecular composition of the core and surface of the particles [17–19].

Results and discussion

The growth of the particles generated by the sol–gel process using silane alkoxides is very dependent on the reaction conditions, i.e. pH, temperature, reaction time, solvent type and the water/monomer molar ratio (r) [3, 7]. In order to obtain the organophilic nanospheres, the reactions were first carried out using the monomer, water and a catalyst in predetermined conditions (growth step), followed by the second step, the addition of monofunctional compounds capable of interrupting the growth of the particles (termination step), introducing nonpolar groups on the surface of the nanospheres. These groups allow better interaction of the nanospheres with hydrocarbons, rendering them hydrophobic. The possible reactions and structures that occur in the growth and termination steps of the particles are presented in Scheme 1.

In the first step of the process, the alkoxysilane monomer is hydrolyzed by molecules of water, generating very small spherical particles that have a great number of hydroxyl groups on their surface. This large number of hydroxyl groups can cause interparticle reactions, resulting in the formation of aggregates of particles with a larger size and which are insoluble in the reaction medium.

To avoid the interparticle links, a second termination step was used. In this study, two types of terminators were used: TMCS and TMES. These terminators contain chlorine atoms or an alkoxide group capable of reacting with the hydroxyl groups, thus reducing the polarity of the particle surface [20].

In the sol–gel process based on the hydrolysis of alkoxysilanes, the H_2O/Si molar ratio (r) varies from 1 up to 25 [6]. It is reported in the literature that under alkaline conditions the rate of the hydrolysis reaction

$$\equiv \mathrm{Si{-}OR} + \mathrm{H_2O} \rightarrow \equiv \mathrm{Si{-}OH} + \mathrm{ROH} \qquad (1)$$

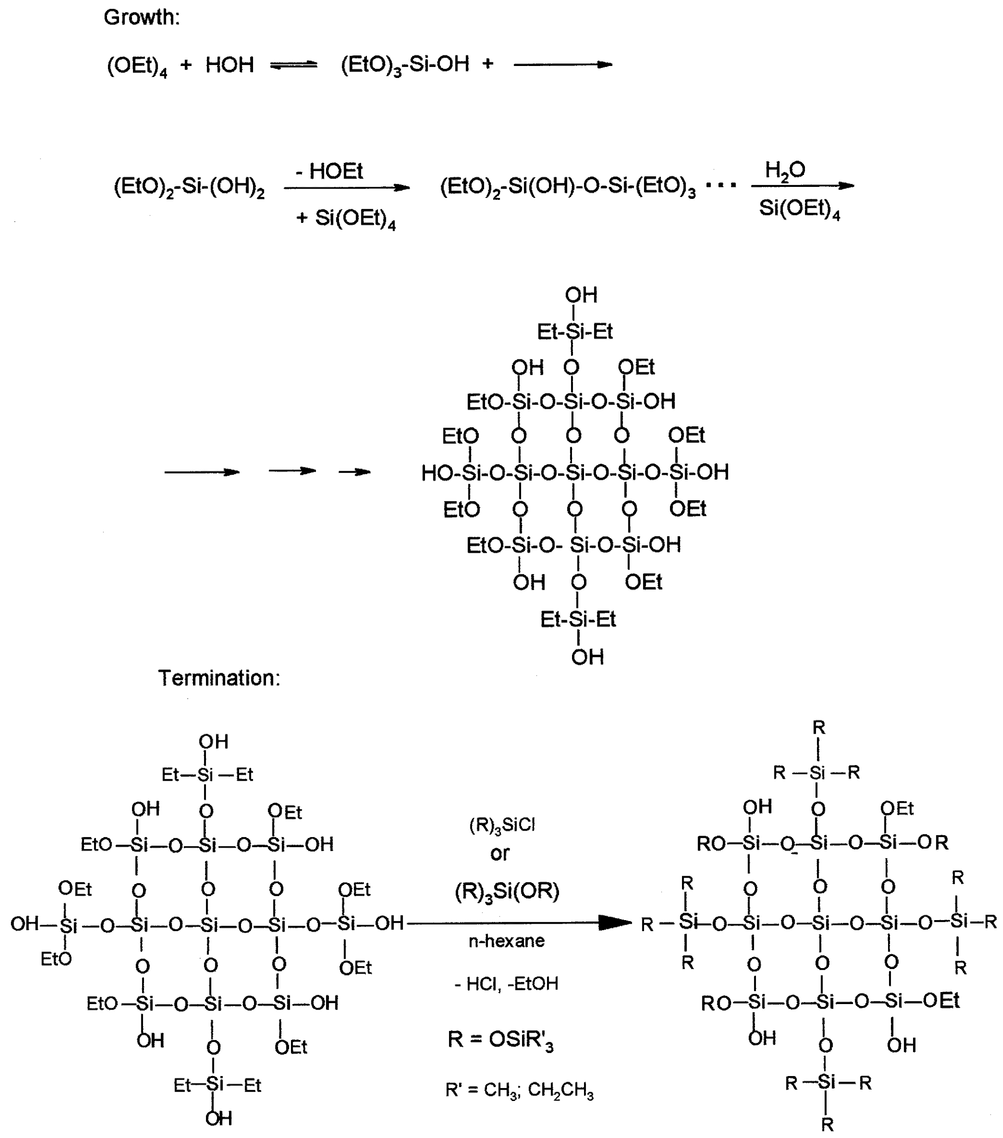
is dependent on the value of r. With regard to the value of r, reaction systems are usually classified in three types: low ($r \geq 0.3$), medium ($r \cong 4$) and high ($r \geq 10$). An increase in r promotes the acceleration of the hydrolysis reaction and decreases the reaction time [6]. The homopolymerization reactions described here were carried out using a value of r close to that of the high reaction system ($r = 8.4$) in order to have shorter reaction times for the growth step.

Effect of the reaction time

The effect of the time of the growth step on the structure of the nanospheres formed is seen in Table 1, which summarizes the results for two series of experiments where the concentration of terminator and reaction time were varied. The data show that the size of the hydrophobic particles increases when the reaction time increases. The values for the number-average particle diameter (D_n) changed from 10.0 to 126 nm, while the particle size dispersion index (D_w/D_n) varied from 1.03 to 1.32. The value of D_w/D_n was directly related to D_n.

For low terminator concentrations (0.23 mol/l), fewer than 24% of the particles dispersed in hexane. When the $(CH_3)_3SiCl$ concentration was increased, the percentage of particles dispersible in hexane was greater than 60% in 4 h of reaction.

From the experiments, it was also possible to conclude that in 20 min of reaction, there was already a high level of conversion, characterized by the large amount of solid product obtained. At that short reaction time the particles had the smallest diameter (10.7 nm). With an increase in reaction time, it is possible that these



Scheme 1 Reactions in the growth and termination stages of nanospheres from the sol–gel process

particles interact with each other, forming larger diameter particles–aggregates, which are insoluble in organic nonpolar solvents. This aggregation scheme would explain the increase in the insoluble fraction in hexane with the increase of the reaction time. Thus, if the aggregation process takes place in the growth step, the termination step has little influence on the dispersion of the particles.

Characterization by IR spectroscopy

The IR spectra of Aerosil (commercial silica) and of the organophilic nanospheres of samples 7/32 and 7/34 are shown in Fig. 1. For Aerosil, three absorption bands appeared between 600 and 4000 cm^{-1}. They correspond to Si—OH (810 and 3450 cm^{-1}), Si—O—Si (1100 cm^{-1}) and absorbed H_2O (1640 cm^{-1}) [9, 18]. The effect of the reaction time on the structure of the particles can be visualized through the spectra of 7/32 and 7/34. In sample 7/32, whose time in the growth step of the particle was 2 h, the bands of Si—OH at 810 cm^{-1} and of Si—O—Si at 1100 cm^{-1} are very weak, indicating that the nucleus of the particle was still in formation. The spectrum also includes a strong band at 1400 cm^{-1} (Si—CH_3), indicative of a high concentration of the —CH_3 group.

The bands of Si–OH (800 and 940 cm^{-1}) are observed in sample 7/34 after 6 h of reaction along with a very intense band at 1100 cm^{-1}. This result indicates that the nucleus of the particle is formed by Si—O—Si bonds. The spectrum also includes an absorption band at 1400 cm^{-1},

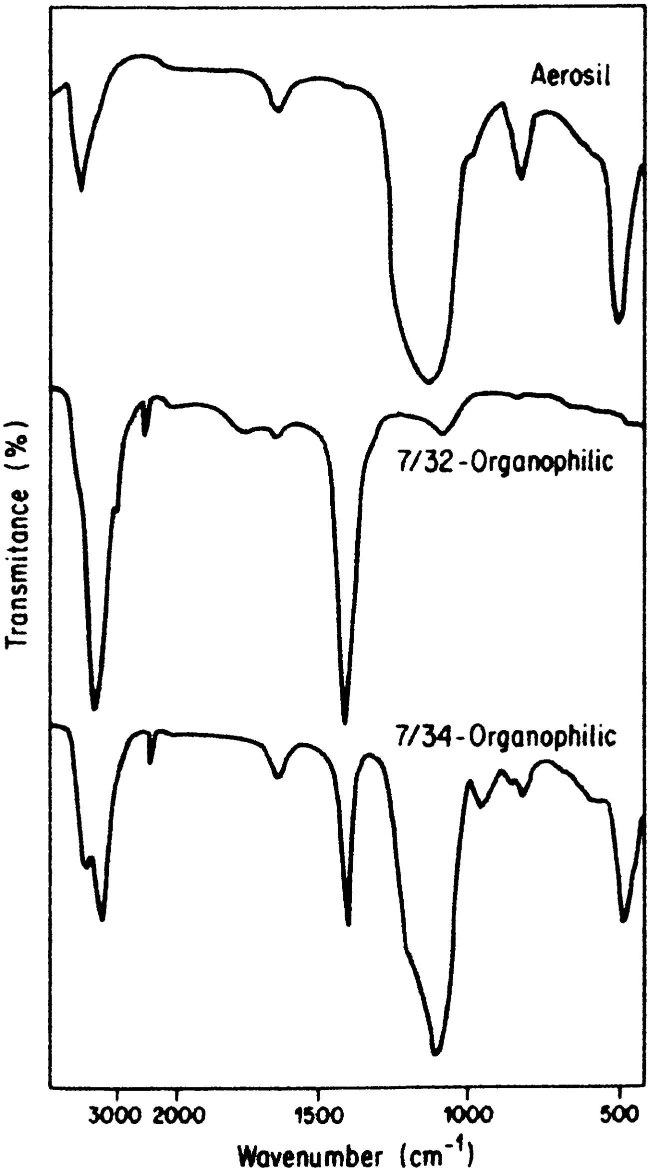


Fig. 1 Fourier transform (FT) IR spectra of Aerosil- and hexane-dispersed fraction of samples 7/32 and 7/34

which is less intense than in sample 7/32, which indicates that the CH_3 superficial/SiO ratio decreased. In spite of this reduction, the amount of CH_3 on the surface seems to be still enough to maintain the particles dispersed in hexane. The results suggest that between 2 and 6 h of reaction there is no significant increase in particle size, but that there is a change in the chemical structure.

The spectrum of sample 7/34 with D_n of about 40 nm was very similar to the spectrum of Aerosil, except for the presence of a weak $-CH_3$ band at 1400 cm^{-1}. This result suggests that the reaction time of 24 h promotes significant growth of the particle, but in this case it has on its surface a smaller amount of OH capable of reacting with the terminator. On the basis of these observations nanospheres with particle size up to 40 nm can be dispersed in hexane.

Effect of the terminator

The function of the terminator in the reaction is to interrupt the growth of the particles and to provide the introduction of $-Si(CH_3)_3$ groups on the surface of the nanospheres, rendering them hydrophobic, according to Scheme 1. The reaction conditions can provide fast growth of the spheres, with structures with larger diameters being formed which affect the desired dispersion. Owing to the larger particle size, nanospheres can be insoluble even if they contain a large number of nonpolar groups on their surface.

The results of the effect of terminator concentration used in the preparation of organophilic particles from TEOS, H_2O and NH_4OH are summarized in Table 2. It shows that the best concentration of TMCS was 0.67 mol/l. From the results it was concluded that the particle dispersibility is directly proportional to the terminator concentration.

It is important to point out that the base used in the termination step of samples 6, 7 and 8 was conjugated with the increase in the terminator concentration. In the termination step, HCl forms according Eq. (2). The acid must be neutralized by a base, in this case NH_4OH, forming a salt (NH_4Cl), which was removed from the reaction medium at the end of the process by washing with water.

$$\equiv Si{-}OH + ClSi(CH_3)_3 \rightarrow \equiv Si{-}O{-}Si(CH_3)_3 + HCl \qquad (2)$$

The NH_4OH used corrects the mediium acidity, which is increased by HCl formation. At the initial step of growth, the concentration of the catalyst (NH_4OH) was constant and equal to 0.1 mol/l.

A comparison was made between the two types of terminator used in these homopolymerization reactions. Three different reaction times were used: 20, 40 and 60 min. The results are summarized for two terminators in Table 3.

The highest values of the percentage of organophilic particles were obtained when $(CH_3)_3SiCl$ was used as the terminator. This result can be explained by considering the higher reactivity of the chlorine-containing compound with hydroxyl groups when compared with the monoalkoxysilane.

In order to obtain more information on the structure of the insoluble material, the hexane insoluble fraction of sample 2/6 was submitted to ultrasound treatment in ethanol and the resulting dispersed and nondispersed particles in this solvent were analyzed by FTIR spectroscopy.

The spectra of the soluble fractions of sample 2/6 obtained after ultrasound treatment for 15 min are presented in Fig. 2. The spectrum of the dispersed fraction in ethanol had absorption bands indicative of the presence of surface OH at 3450 and 800 cm^{-1}, plus bands of Si—O—Si at 1100 cm^{-1} and Si—O—CH_2CH_3 at 950 cm^{-1}. Another band at 1640 cm^{-1}, due to molecular water absorption, also appeared. The FTIR spectrum of the insoluble fraction after ultrasound treatment revealed bands at 3450, 1640, 955 and 800 cm^{-1}, suggesting that the structures of the dispersed and the nondispersed fractions in ethanol are very similar to each other. Both spectra are also quite similar to the spectrum of the commercial silica Aerosil (Fig. 1). The results also showed that the nondispersed fraction contained a high amount of OH and fragments of nonreacted ethoxysilane. These OH groups should also favor interparticle interactions through hydrogen bonding, resulting in the formation of aggregates of nanospheres with dimensions large enough to decrease the dispersibility. For the latter synthesis conditions, it appears that low levels of reactions of the surface hydroxyl groups and the terminator occurred.

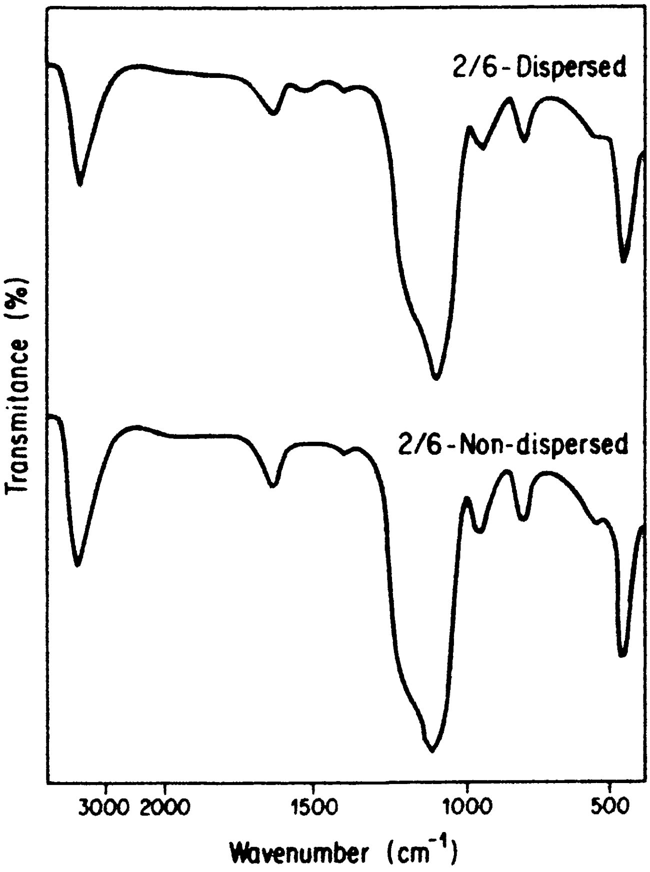


Fig. 2 FTIR spectra of ethanol-dispersed and nondispersed particles obtained after ultrasound treatment of the hexane insoluble fraction of sample 2/6

Effect of the temperature in the termination step

The influence of the temperature of the termination step on the number of organophilic particles was also investigated in the case of TMES. The results obtained when termination was accomplished at 50 °C and at room temperature (23 °C) are compared in Table 4. The table indicates that increasing the temperature in the termination step decreased the fraction of particles dispersed in hexane to very low values (0.020–0.61%). At room temperature (23 °C), those values were from 6.5 to 14.9% and represents an increase of 2,400–32,500 times. Such a result can be explained considering the higher reactivity of the reaction components at higher temperatures. The reaction at higher temperatures may have provided an increase in the number of interparticle connections by condensation reactions, resulting in the formation of insoluble aggregates of nanospheres with size larger than the critical size (about 100 nm). A similar result was also obtained even with highly basic media, as in the case of sample 6/30, whose concentration of NH_4OH was 69.3 mol/l. D_n of the organophilic particles generated using a termination temperature of 50 °C was larger, reaching 73.4 nm. D_w/D_n observed for these conditions was very narrow, varying from 1.08 to 1.39, showing that the dispersed particles obtained are quite homogeneous with respect to size.

Table 4 also shows that the termination step time also has a significant influence on the amount of dispersible product. The percentage of organophilic material increased when the reaction time was increased. Nevertheless, even after 48 h the fraction dispersed in hexane is still very small (0.61%) when the termination is carried out at 50 °C. Therefore, low termination temperatures favor the formation of dispersible particles.

Conclusions

Hydrocarbon dispersion of nanospherical organophilic silica with diameter from about 10 to 130 nm can be obtained by TEOS homopolymerization using the sol–gel process catalyzed by a base and a terminator. Homopolymerization for the conditions used in this study did not result in percentages of hydrophobic particles greater than 62%. The reaction time of the particle growth step is decisive in determining the size of the particles. Increased reaction times cause an increase in particle size and its precipitation. An increase in the terminator concentration promotes an increase in the amount of hexane-dispersible product. Chlorinated terminators are more efficient than alkoxides with respect to increasing the hydrocarbon-dispersible fraction. Lower temperatures in the termination step favor an increase in the number of organophilic particles.

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