HOLLOW SILICA PARTICLES FROM SILICA SOL

Cite this: *INEOS OPEN*, **2024**, *7 (1–3)*, 11–12
DOI: 10.32931/io2406a

Received 20 May 2024,
Accepted 30 May 2024

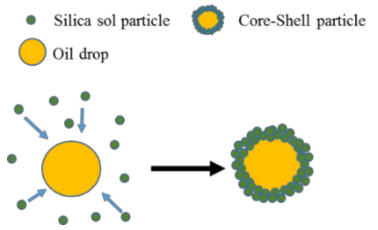
http://ineosopen.org

K. M. Borisov,*[a,b] D. M. Borisova,[a,b] A. A. Kalinina,[a,b] and A. M. Muzafarov[a,b]

[a] *Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, str. 1, Moscow, 119334 Russia*
[b] *Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences, ul. Profsoyuznaya 70, Moscow, 117393 Russia*

Abstract

The possibility to obtain hollow particles using silica sol as a precursor of a silica shell at different pH values of a D4 emulsion in water is studied. It is shown that the yield of particles, their structure and sizes strongly depend on the pH value.



Key words: hollow particles, silica sol, emulsions.

Introduction

Hollow micro- and nanospheres have a broad application scope, including thermal insulation [1–3], lithium-ion batteries [4–6], and biomedical applications [7, 8]. The most extensively used hollow capsules are those made of silica shells, the advantage of which is the simplicity and diversity of methods for their formation, as well as the presence of reactive hydroxy groups, capable of further modification of particles and providing the ability to change the properties of the silica surface in a wide range.

It was shown earlier [9] that the use of silica sol as a precursor allows for obtaining hollow particles at a high speed. Due to their small sizes and surface, which contains hydroxy groups able to react with each other, these particles can form a mechanically stable shell. This work is a continuation of our studies and is devoted to the evaluation of the effect of the dispersion medium pH on the formation of hollow capsules using silica sol as a shell precursor.

Results and discussion

Silica sol was synthesized according to the known procedure [10, 11]. Then octamethylcyclotetrasiloxane (D4) was used as a dispersed phase to prepare an oil-in-water emulsion (water/D4 ratio = 175:1 parts by weight). The possibility of the formation of hollow particles using silica sol as a shell precursor was studied at the emulsion pH values of 4, 7, and 10.4, which was controlled by adding acetic acid or an aqueous ammonia solution. Dispersion was carried out at 10000 rpm for 5 min using a mechanical disperser (IKA ULTRA-TURRAX T 50), after which silica sol was added at an amount of 1 and 1.5 parts by weight per 1 part by weight of D4 under continuous dispersion. Immediately after that, the mixture was centrifuged at 11000 rpm for 30 min, rinsed 3 times with water, and dried at room temperature under vacuum.

At the first stage, the behavior of the D4 silica sol system in water with a neutral pH value was investigated. Regardless of the D4/silica sol ratio, multiporous particles with a diameter of ~1.5 μm were obtained in 35–40%. The results of scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis showed (Fig. 1a,b) that these particles are polydisperse, which was confirmed by the results of size analysis from photographs (see Fig. S1 in the Electronic supplementary information (ESI)) and have many macropores with the sizes from 30 to 150 nm. The bulk density of these samples was 0.88 and 0.91 g/cm^3 at the D4/silica sol ratio of 1:1 and 1:1.5, respectively.

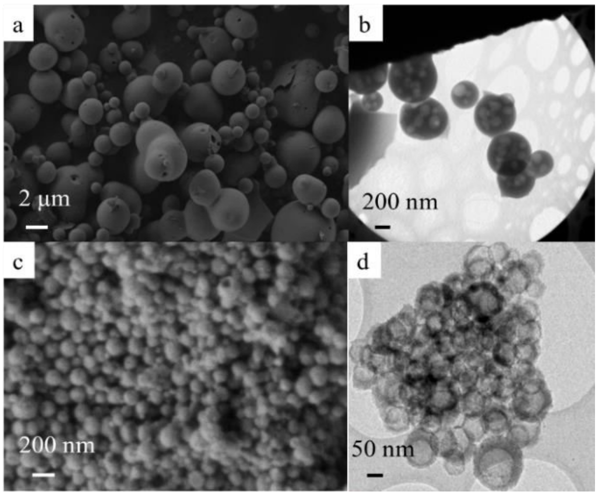


Figure 1. SEM (***a*** and ***c***) and TEM (***b*** and ***d***) micrographs of the particles obtained in neutral (***a*** and ***b***) and basic (***c*** and ***d***) media.

When silica sol was added to the acidic emulsion of D4 in water (pH = 4), particles with a structure and sizes (see Fig. S2 in the ESI) similar to those of the emulsion with pH = 7 were obtained after centrifugation. The similarity of the results upon application of the acidic and neutral emulsions can probably be explained by the fact that, after adding silica sol to the D4 emulsion in water, the medium becomes acidic in both cases due to acetyl chloride and its hydrolysis products remaining in the silica sol after its production. As a result, the medium pH after adding silica sol was 3.4 in the case of the pre-acidified emulsion of D4 and 4.5 in the case of the D4 emulsion with a neutral pH value. The bulk density of the samples was 0.82 and 0.65 g/cm^3, respectively. The yields of hollow particles ranged within 35–40%. Due to the rapid shell formation, several drops of the dispersed phase of the initial emulsion may probably enter the particle formation zone, which explains the macroporous structure of the particles.

In the case of the basic D4 emulsion (pH = 10.4), hollow particles were formed, but their yield was significantly lower than in the analogous experiments in acidic and neutral media, composing only 2–10% after centrifugation. This is likely to be caused by the rapid condensation of hydroxy groups on the particle surface and, as a result, the formation of agglomerates instead of hollow particles. Despite the low yield, the resulting hollow particles were fairly monodisperse (Figs. 1c,d) and their sizes differed significantly for the samples obtained in acidic and neutral media (see Fig. S3 in the ESI). This difference in sizes may be due to the negative charge formed on the particles under basic conditions, as a consequence of which the stabilization of smaller particles becomes possible, although the rapid condensation of OH groups prevails over stabilization. Independent of the D4/silica sol ratio, the particles had the same structure and sizes. The general characteristics of all the particles obtained are given in Table 1 (see also Table S1 in the ESI).

Table 1. Sizes and yields of the resulting particles

Sample	pH of the D4 aq. emulsion	D4/silica sol ratio	Particle sizes, μm	Yield of hollow particles, %
1	4	1:1	1.64	35–40
2	4	1:1.5	1.49	35–40
3	7	1:1	1.3	35–40
4	7	1:1.5	1.46	35–40
5	10.4	1:1	0.115	2–10
6	10.4	1:1.5	0.11	2–10

In all cases, the yield of hollow particles after centrifugation was below 45%. The remaining part of silica formed a suspension in a mixture of water and THF. Drying of this mixture afforded silica agglomerates (see Fig. S4 in the ESI), which were observed for all of the samples.

Conclusions

The effect of the emulsion pH on the possibility of the formation of hollow particles using silica sol as a precursor of a silica shell was studied. The possibility of obtaining macroporous and hollow particles was demonstrated. The resulting particles can be used as fillers for the creation of materials with low thermal conductivity.

Acknowledgements

This work was supported by the Russian Science Foundation (project no. 22-43-04439).

The GPC analysis of the silica sol precursor was performed with financial support from the Ministry of Science and Higher Education of the Russian Federation using the equipment of the Collaborative Access Center "Center for Polymer Research" of ISPM RAS (FFSM-2024-0001).

Corresponding author

* E-mail: bora.91@mail.ru (K. M. Borisov).

Electronic supplementary information

Electronic supplementary information (ESI) available online: the synthetic procedures for the hollow particles, the size distribution of the particles, the results of SEM analysis, general characteristics of the particles. For ESI, see DOI: 10.32931/io2406a.

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