Journal of Thermal Analysis and Calorimetry, Vol. 93 (2008) 3, 783–787

PREPARATION OF MICROSPHERICAL GRANULES FROM AEROSILOGELS
The way of spray drying in overheated water steam

Jadwiga Skubiszewska-Zięba[1]* *and V. Sydorchuk*[2]

[1]Faculty of Chemistry, Maria Curie-Skłodowska University, 20-031 Lublin, Poland
[2]Institute for Sorption and Problems of Endoecology, Naumov St. 13, 252164 Kiev, Ukraine

The influence of the conditions of aerosil dispersion spray drying process in the medium of overheated water steam on the formation of microspheric granules and their porous structure was studied. Water and ammonium solutions as aerosil particles dispersing agents and water steam and air as heat carriers were used. It was stated that the effects of spray drying depend on the kind of dispersing medium and on the conditions of atmosphere and temperature at which drying and forming of aerosilogel granules takes place.

Keywords: *aerosilogels, aerosils, HTT, porous structure, spray drying*

Introduction

As it is known, high purity pyrogenic oxides, including aerosils, are perspective materials for preparation of adsorbents, column packings for HPLC, etc. They are also used as catalyst carriers [1] and as polymer fillers [2].

On the basis of such oxides, manufactured in the form of powders of very small size particles (a few-dozen nanometres), formation of granules and objects of different shapes and dimensions is possible [3]. During such processes the homogeneous mesoporous structures are formed [3–5]. One of the methods of silica microspheric granules preparation which e.g. can be used in heterogeneous catalysis or in liquid chromatography, where particles over 100 μm are required, may be spray drying [6–8]. This method is also very useful in preparation of drugs with better thermal stability [9, 10].

In papers [11–15], the advantages of spray drying of solids in the medium of overheated water steam in comparison to air as a heat carrier are presented. Due to the lower moisture gradient between the heat carrier and the dried material, the drying process proceeds under milder conditions. Moreover, a drying rate is increased and real consumption of heat is reduced, because the heat capacity of water steam is 20–30% higher than that of air. It also refers to drying of porous materials [16]. Another technical advantage of drying in overheated water steam is the possibility of application of heat carrier closed circulation in the system [8, 11, 17, 18]. The characteristic feature of spray drying is short residence time of dried particles in the camera. It is about 5–50 s [11, 19, 20].

It is known [21, 22] that during the action of water steam on the silica gels and xerogels at the increased temperature (hydrothermal or thermo-steam treatment) the essential changes of their porous structure parameters take place. It is caused by intensely running processes of silica transfer [23–27]. It may be supposed that in the drying process of silica dispersions by overheated water steam the conditions of hydrothermal modification are fulfilled to some extent. In papers [21, 28] some data concerning drying of silica hydrogel (at 120°C for 4 h) in overheated water steam are presented. As a result the xerogel of low apparent density was prepared. However, literature does not provide any information about spray drying of silica suspensions where water steam would be used as a heat carrier. The authors of papers [4, 12] suggested that during silica dispersions spray drying in the overheated water steam silica particles can undergo additional (however, in a short time) hydrothermal and thermo-steam treatment.

In this paper the results of experimental verification of the above mentioned hypothesis are presented. The aim of the experiments was to investigate the influence of aerosil dispersion spray drying conditions on the properties of formed microspheric silica granules. In particular, the influence of the kind of dispersing medium and the heat carrier on the effects of spray drying was taken into account.

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* Author for correspondence: jskubisz@hermes.umcs.lublin.pl

1388–6150/$20.00
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Springer, Dordrecht, The Netherlands

Experimental

Two aerosils A-175 and A-380 ('Oriana' Kalush, Ukraine) were used as the initial silica materials (specific surface areas S=219 and 364 m^2 g^{-1} and primary particle sizes of 12.5 and 7 nm, respectively). On the basis of these materials adequate dispersions in distilled water and in the ammonia solutions of 2 and 5% were prepared. A concentration of aerosil in a given dispersion was 15% *w*/*w*, which for such systems corresponds to critical concentration for structurization [29]. The dispersions with such concentrations of solid phase possess the most favourable structural–mechanical and rheological characteristics for the granulation process [30].

The spray drying in the medium of water steam at 300–600°C was performed using the laboratory devise described in paper [31]. The residence time of the particles in a drying chamber was about 30 s. The specific surface area S was measured by the method of argon heat desorption [32] using the GCh-1 apparatus (Chromatograph, Russia). The total pore volume V_Σ, the volume distribution of pores in the function of their radius were calculated on the basis of mercury porosimetry data obtained by using of PA-3M apparatus (Carlo Erba, Italy).

The fractional analysis of microspheric aerosilogels was performed by using the microscope 'Optima' (Germany). For the quantitative analysis there were taken about 100–150 granules. From the obtained data there were constructed histograms – quantitative distributions of granules in the function of their sizes D and the average granule size D_{ave} was calculated.

Atomic force microscopic (AFM) images were obtained by means of a NanoScope III (Digital Instruments, USA) apparatus using a Tapping Mode AFM measurement technique.

Results and discussion

Table 1 presents the structural characteristics of prepared aerosilogels. For comparison there were put the parameters of two aerosilogel samples (numbered as 0) prepared by dispersion in water and dried in air without spray drying. As it is seen even very short contact time (about 30 s) of aerosilogel dispersion drops with the water steam leads to quite significant changes in initial aerosils (A-175 and A-380) porous structure parameters. In general, independently on the kind of dispersion medium and heat carrier the values of specific surface areas of the initial aerosils decrease significantly. At the same time total pore volume V_Σ increases. These changes depend on the conditions of drying procedure.

In the last column of Table 1 the values of globule diameters D_g, which are the main components of silica frame, are compared. They were calculated on the basis of equation [33]:

$$D_g=6\cdot 10^3/\rho S \quad (1)$$

where S is specific surface area m^2 g^{-1} and ρ=2.2 g cm^{-3} is the density of amorphous silica [21].

Table 1 Influence of spray drying on structural properties of microspherical aerosilogels

No.	Aerosil	Medium	Temp./°C	S/m^2 g^{-1}	V_Σ/cm^3 g^{-1}	d_p/nm	D_{ave}/μm	D_g/nm
0	A-175	water	20	204	1.74	42.0	–	13.4
1	A-175	water/air*	400	191	1.70	37.2	17.6	14.3
2	A-175	water	400	170	1.82	42.8	12.3	16.0
3	A-175	1% ammonia	400	154	2.02	54.0	12.4	17.7
4	A-175	2% ammonia	400	125	2.68	88.5	13.1	21.8
5	A-175	5% ammonia	400	141	2.48	64.8	12.9	19.3
6	A-175	2% ammonia	500	98	3.07	122.0	12.8	27.8
7	A-175	2% ammonia	600	85	3.40	160.0	13.0	32.1
0	A-380	water	20	350	1.56	18.0	–	7.8
8	A-380	water	400	332	1.65	21.6	13.1	8.2
9	A-380	water	500	314	2.12	28.8	11.2	8.7
10	A-380	water	600	290	2.88	41.5	10.6	9.4
11	A-380	2% ammonia	400	256	2.21	35.0	8.5	10.7
12	A-380	2% ammonia	500	240	2.15	34.2	12.4	11.4
13	A-380	2% ammonia	600	238	2.16	38.1	13.3	11.5
14	A-380	5% ammonia	600	277	2.01	29.6	9.3	9.8

S – specific surface area, V_Σ – total pore volume, d_p – average pore diameter, D_{ave} – average microsphere diameters, D_g – globule sizes; *water – dispersing medium, air – heat carrier

As it is seen, independently on the conditions of the drying process the globule dimensions of both aerosils increase. The increase of D_g values may be connected, similarly to common hydrothermal modification of silica adsorbents, with the processes of silica mass transfer. Such processes are based on the reactions of small aerosil particles polymerization with the formation of orthosilicic acids which next are recondensed on the surface of large particles in the sites of their contacts [27]:

$$(SiO_2)_n+2H_2O=(SiO_2)_{n-1}+Si(OH)_4 \qquad (2)$$

The direction of mass transfer of orthosilica acid is determined by the value of surface energy which depends on the dimensions of primary particles (globules). The smallest silica particles which possess the maximal surface energy are dissolved first. The dissolved silica is transported and deposited in other places with lower energy which is promoted firstly by very high temperature of water steam, which strongly acts on the dispersed suspension. Secondly, by the catalytic impact of ammonia on the course of silica mass transfer processes (being the reason for changes in silica porosity) [21, 22] and thirdly – high degree of spray dispersion, which immediately causes quick heating of its 'drops' along all their cross sections. As a result the decondensation processes in aerosil primary particles and recondensation of silicic acid on their surface run at great speed, causing their adhesion which in the consequence leads to the formation of porous microspherical granules. Moreover, thanks to this process the globules homogenization, in respect of their sizes, takes place and silica material structure becomes more regular. Figure 1 presents AFM images of initial fumed silica A-380 and aerosilogel prepared on its basis by spray drying in overheated water steam at 400°C. As it is known, aerosil has a free dispersion character with primary particles of different globule sizes and grouped in loose aggregates and agglomerates (Fig. 1a). When, such material is subjected to hydrothermal treatment its structure is dense with more regular particle sizes (Fig. 1b).

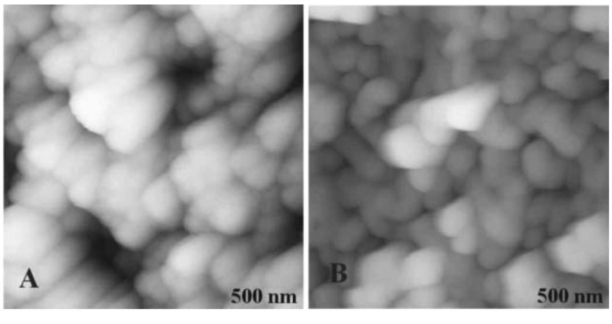

Fig. 1 AFM images for A – initial fumed silica, aerosil A-380 and B – aerosilogel microsphere prepared by spray drying at temperature 400°C in overheated water steam

For comparison, it is worth reporting the literature data concerning the common (in the autoclave) hydrothermal treatment of silica gels. Thus, with such a modification at temperature 100–300°C, as a rule, about 3–5 h are required to achieve similar changes of S values as presented in Table 1 [26]. However, in the case of larger semi-industrial autoclaves used in the modification, due to poor heat conductivity of the silica, it is often necessary to prolong the time of modification to 24 h to obtain homogeneous product with respect to its properties [4, 12].

It follows from the data presented in Table 1 and in Fig. 2 that with the increasing temperature of water steam used as a heat carrier, the specific surface area of the obtained microspheric aerosilogels decreases, but their pore volumes and sizes increase (compare the data for samples 8, 9 and 10 in Table 1). Such regularity is typical for hydrothermal modification of silica hydrogels [3]. The composition of dispersing phase has a significant impact on structural parameters of microspheric granules, which is seen by comparing suitable data for samples 3, 4 and 5 (Table 1). The authors of paper [34] stated that the composition of gas phase influences significantly the speed of aerosils hydrothermal modification (HTT). Application of H_2O+NH_3 mixture as a modifying medium allows to decrease the temperature and pressure during silica adsorbents preparation with a low specific surface area S. Such effects are evident comparing the data in Table 1 for samples 2 and 3, 8 and 11, 9 and 12 as well as 10 and 13. The presence of low quantities of ammonia (1–2%) causes significant acceleration of increasing globule sizes processes (D_g) and in a consequence, the space between them (pore volumes V_Σ) and decreasing of S value. For example, by comparison of samples 8 and 11 it follows that their S and V_Σ values differ by 76 m^2 g^{-1} and 0.56 cm^3 g^{-1}, respectively. Such differences in the

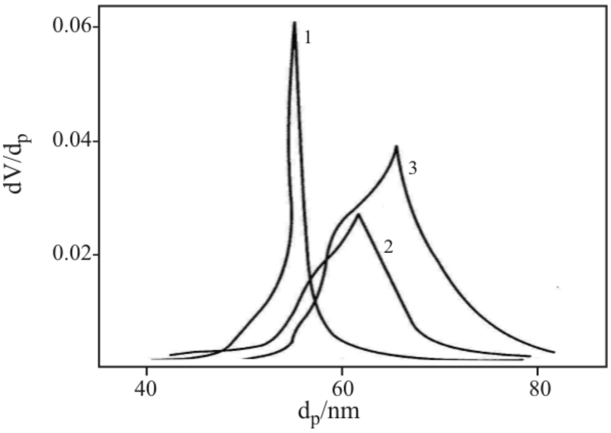

Fig. 2 Distribution of pore volumes in respect of their sizes for aerosilogel samples (Table 1) 1 – 8, 2 – 9 and 3 – 5

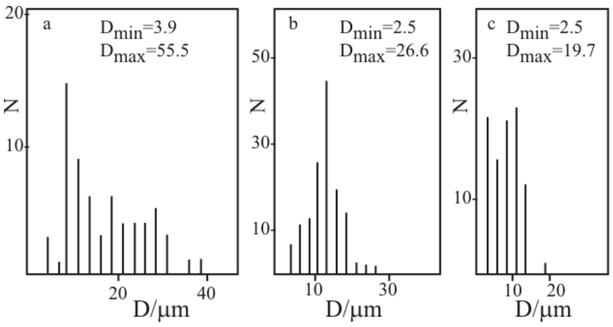

Fig. 3 The histograms of quantitative distributions of granules in the function of their sizes *D* for samples a – 1, b – 5 and c – 11

values of mentioned parameters can not be achieved by carrying out the aerosils water dispersions drying process without the addition of ammonia at a temperature higher by 100°C (compare samples 8 and 9).

For higher concentrations of ammonia (5%) there is observed a comparatively low relative increase of *S* value and an appropriate decrease of V_{Σ} and d_p (samples 5 and 14 in Table 1), which is caused by partial peptisation of hydrogel formed by the dispersed aerosil.

It should be pointed out that the application of water steam overheated to 300–600°C as a heat carrier instead of air allows to ensure milder conditions for removal of liquid from the dispersion droplets and, in its consequence, elimination of sites with strong tensions in the structure of the aerosilogel. It can lead to some strengthening of formed granules, which is taken into consideration in [21]. On the other hand due to high temperature of heat carrier and intermicellar liquid in gel, this liquid surface tension decreases. It causes the formation of pores of very large volume (over 3 $cm^3 g^{-1}$) in the microspherical granules. In such a manner the porosity of prepared silicas becomes close to aerosilogels [21, 35].

As follows from the data presented in column 8 of Table 1 and in Fig. 3, during spray drying in the overheated water steam more fine and uniform microspheres, in respect of their sizes, are formed compared to drying in hot air (compare the differences in granule sizes from D_{min} to D_{max} for both cases – Fig. 3). It gives the evidence of technological superiority of drying in the overheated water steam.

It should be also pointed out that during drying of dispersion, the water vapour is formed which after condensation may be used again for the preparation of new portions of aerosil dispersions, i.e. the process of microsphers preparation may be a closed cycle.

Conclusions

- There were shown certain new possibilities of microspheric silicas preparation on the basis of aerosils by spray drying.
- Application of overheated water steam during spray drying of aerosil dispersions allows to obtain uniform microspheric aerosilogels, in respect to their fraction composition, with the granule sizes of 10–12 μm.
- During spray drying decondensation and recondensation processes of primary aerosil globules play an important role, leading to globule diameter increase and their coalescence and as a result the uniform microspheric granules are formed with high pore volumes to over 3 $cm^3 g^{-1}$. The presence of small quantity of ammonia in the dispersing medium accelerates the processes of globule growing, which influences the structural parameters of the prepared granules.
- In the spray drying process carried out with respect to microspheric silica granules preparation the air is a worse heat conductor than the water steam. As a result, under the same conditions the globule growing processes and the same the changes of *S*, V_{Σ} and D_{ave} are poorer when air is applied as the heat carrier. Water steam plays the role not only as a good heat carrier but also it takes part in the processes of decondensation and recondensation of silicic acid.

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DOI: 10.1007/s10973-008-9202-0