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Properties and Advantages of Powdered Ice-Forming Reagents Based on Nanoscale Silica

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ABSTRACT

A series of powder ice-forming reagents based on the principle of Levilites was synthesized by gas-phase solvate-stimulated adsorption modification (GSSAM) of highly disperse nanoscale silica with silver iodide and phloroglucinol. Lab studies of the prepared materials showed that ice-forming activity per mass unit of AgI and phloroglucinol deposited onto a surface of silica nanoparticles according to the GSSAM technology corresponds to the values of native preparations. In this case, the best sample containing AgI is superior in the efficiency to known AD-1 reagent.

***Keywords*: Ice-forming reagents, principle of Levilites, nanosilica, adsorption modification.**

Introduction

Active influence on clouds and fogs carried out in order to (i) cause precipitation from the clouds; (ii) dispersal of fogs over the runway of airports; and (iii) suppress hail [1, 2].

The main way to influence clouds containing supercooled water droplets is to create ice crystals in them, which help accelerate the process of precipitation formation. Crystallizing and hygroscopic reagents, as well as coolants, are used for seeding clouds [3-7].

The physical basis for the use of crystallizing reagents is the ability of their aerosols to create ice crystals in supercooled clouds. Aerosols of many inorganic and organic substances possess this property, but aerosols of silver (AgI) and lead (PbI_2) iodides have the most effective crystallizing ability [8].

In practice, the problem of using ice-forming reagents is largely reduced to the issue of obtaining aerosols with the required structural parameters by using different dispersion methods.

For the dispersion of AgI, the following methods are mainly used: 1) explosions of AgI containing composition in pyrotechnic flares in rockets, 2) burning AgI containing solutions in a generator of particles attached to an airplane.

In the first case, the pyrotechnic compositions containing the active reagent (AgI) and iodination components (KI, NH_4I, NH_4IO_3, $C_7O_2H_5I$) are used to contribute increasing ice-forming efficiency of the composites. Typically, pyrotechnic compositions based on silver iodide and perchlorate or ammonium nitrate at AgI content of 2 to 40% are used. The formation of the ice-forming aerosol occurs due to high-temperature (from 700 to 1400 ^{o}C) sublimation of AgI, followed by the condensation of Ag and I ions on particles consisting of products of burning pyrotechnic composition. Therefore, such an aerosol is often called "thermocondensation aerosol".

The second method to prepare a thermocondensation aerosol is burning acetone solution of AgI. This method is used for aircraft seeding of layered clouds. To improve the solubility of silver iodide and to increase its ice-forming activity, iodides of ammonium and other elements are added to the solution.

The effectiveness of the crystallizing reagents is characterized by several parameters, the most important of which is the yield of active ice-forming nuclei per gram of composition. The yield of ice-forming nuclei using a thermocondensation aerosol depends on many factors: the AgI content, the activating components and their physicochemical properties; design features of the aerosol generator; dispersion conditions of the reagent, air humidity; speed of blowing of the generator, etc. [3].

These factors determine the dispersity of the formed aerosol that affect the structure and ice-forming activity. The increase in dispersity leads to an increase in the number of particles per mass unit of the reagent, but too small particles show ice-forming activity only at very low temperature. The formation of large particles leads to the production of an aerosol that is active in the required temperature range (from -5 to -10 °C), but the yield decreases per gram of composition. Therefore, the composition of the crystallizing reagents is specially selected that the formation of an ice-forming aerosol with core-shell particles composed of a core with the combustion products on a surface of which there are fragments of AgI. This ensures the production of sufficiently large particles with a minimum consumption of AgI contained on their surface.

The mentioned above methods for the dispersion of silver iodide are sufficiently effective, but they have a number of technological flaws, in particular, it needs to use dangerous combustible and explosive substances. The shortcomings of the pyrotechnic composition also include the high laboriousness of manufacturing charges and low energy characteristics. Anti-hail rockets containing pyrotechnic compounds have a small payload mass factor due to the lack of unitarity of loading, low efficiency and range.

An alternative to the use of pyrotechnic flares and burning of solutions can be the AgI dispersion method based on the principle of Levilites. It consists in spreading a thin layer of active substance at a surface of particles of a cheap inert highly disperse carrier. It is believed that the use of a highly disperse carrier can significantly increase the yield of ice-forming particles per mass unit of the active substance [9].

In the 80s of the last century, an amorphous, nonporous, highly disperse nanoscale silica (nanosilica) was used as an inert carrier [10]. One gram of such nanosilica with a specific surface area of 300 m^2/g and a bulk density of 50-60 g/dm^3 contains approximately 10^{18} primary particles with a diameter of 9-10 nm. On the surface of the nanoparticles there are free silanol groups ≡Si–OH, which are the main adsorption sites (in an amount of ~0.8 mmol/g) and sorbed water molecules (0.8-1.5 mmol/g or 1.5-2 wt.%) [11]. Due to the high adsorption potential, nanoparticles form such secondary structures as aggregates (50-1000 nm) and agglomerates (1-20 μm), which can disintegrate easily under external action (Fig. 1).

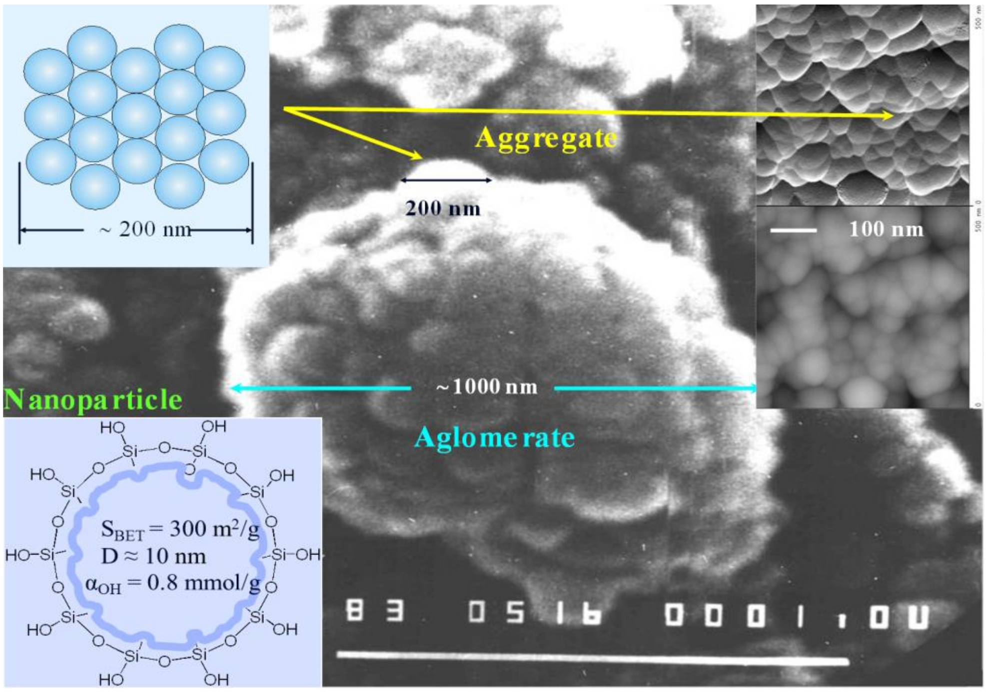


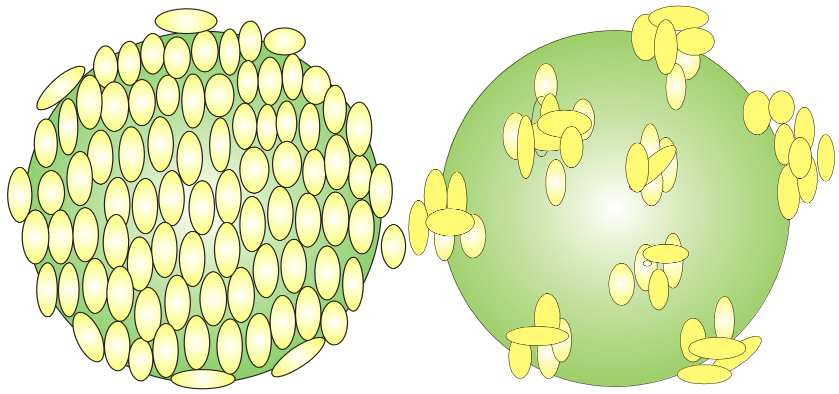
Fig.1. Scheme and microphotographs of nanosilica.

By adsorption modification with the use of vacuum technology, various inorganic and organic substances with ice-forming activity were grafted onto the surface of the nanoparticles. Surface clusters were formed both with pure AgI and additives of other iodides such as ammonium, potassium and calcium [12-14]. As an organic substance, phloroglucinol (1,3,5-trioxibenzene) was used. Two types of structures were created on the surface of nanoparticles: (I) a monomolecular adsorption layer, and (II) phloroglucinol molecules chemically bonded to the surface.

Studies of the ice-forming properties of the prepared reagents were carried out in a laboratory at UkrNIGMI. It was found that the yield of active particles depends on the nature and content of substances possessing ice-forming activity. For synthesized samples, it was varied from 10^{13} g^{-1} in the case of surface clusters with pure AgI to 10^{11} g^{-1} for a monolayer of phloroglucinol. By combination of content of precious metals, synthesis conditions, availability of raw materials, etc., reagents with additives of iodides of other metals could be considered as promising compositions. However, the combination of pulverized highly disperse silica and vacuum technology has made it impossible to convert such a laboratory method for preparation of a new type of crystallizing reagents into a real industrial technology.

Materials and methods

In recent years at the Chuiko Institute of Surface Chemistry of NAS of Ukraine in collaboration with colleagues from other countries, a method has developed for gas-phase solvate-stimulated adsorption modification (GSSAM) of nanosilica with inorganic salts and non-volatile organic compounds that is realized under normal conditions (room temperature and atmospheric pressure) [11, 15-17]. The use of the GSSAM method allows us to form submonolayer, monolayer or multilayer coatings on a surface of silica nanoparticles, as well as individual clusters with any nonvolatile organic compounds or inorganic salts (Fig. 2).



a) monolayer coating b) clusters

Fig. 2. Scheme of possible distribution of molecules at a surface of a silica nanoparticle.

The described synthetic capabilities of the GSSAM method allow us substantial simplification of the formation of a layer or clusters of ice-forming substances on a surface of nanoparticles. As a result, on the basis of the GSSAM method, the laboratory and then pilot technology for preparation of powdered ice-forming reagents based on nanosilica was created in at CISC.

Using a variety of GSSAM technologies including in situ reactions, samples based on nanosilica containing pure AgI and AgI with additions of other iodides, as well as samples containing phloroglucinol in the amount of 1 and 3 layers (Tables 1 and 2) were preparated.

Table 1

Samples of crystallizing reagents based on nanoscale silica with low bulk density

Sample number	Synthesis number	Composition	Bulk density, g/l	Ice crystals yield per 1 g of powder	
				t, °C	
1	M-333	AgI (≈ 10%), nanosilica	80	-12.0	$5.5 \cdot 10^{13}$
				-10.0	$4.46 \cdot 10^{13}$
				-9.0	$4.12 \cdot 10^{13}$
				-8.0	$1.53 \cdot 10^{13}$
				-5.5	$8.1 \cdot 10^{12}$
				-5.0	$6.0 \cdot 10^{12}$
				-4.0	$1.08 \cdot 10^{12}$
				-3.0	$9.66 \cdot 10^{11}$
2	M-335	AgI (≈ 10%), nanosilica	207	-10.0	$2.12 \cdot 10^{13}$
				-6.5	$4.3 \cdot 10^{12}$
				-5.5	$4.02 \cdot 10^{12}$
				-5.5	$3.9 \cdot 10^{12}$
				-5.0	$1.8 \cdot 10^{12}$
				-4.5	$4.84 \cdot 10^{11}$
				-2.4	$< 10^{9}$
3	M-336	AgI (≈ 10%), nanosilica	91	-12.0	$7.82 \cdot 10^{13}$
				-10.0	$5.94 \cdot 10^{13}$
				-10.0	$4.98 \cdot 10^{13}$
				-6.0	$3.6 \cdot 10^{12}$
				-5.5	$3.3 \cdot 10^{12}$
				-5.0	$2.5 \cdot 10^{12}$
				-4.5	$1.23 \cdot 10^{12}$
				-3.6	$3.74 \cdot 10^{11}$
4	M-332	phloroglucinol (≈ 9%), nanosilica	61	-11.0	$2.23 \cdot 10^{13}$
				-10.0	$2.01 \cdot 10^{13}$
				-6.0	$2.81 \cdot 10^{11}$
				-5.0	$1.80 \cdot 10^{11}$
5	M-334	phloroglucinol (≈ 23%), nanosilica	110	-11.0	$3.47 \cdot 10^{13}$
				-10.0	$3.38 \cdot 10^{13}$
				-5.0	$1.67 \cdot 10^{11}$

Table 2

Samples of crystallizing reagents based on nanoscale silica with high bulk density

Synthesis number	Composition		Bulk density, g/l	Note
	Active substance	content, %		
LN-211	AgI	10	377	
LN-212	AgI	10	413	
LN-213	Phloroglucinol	9	267	Monolayer
LN-214	Phloroglucinol	23	279	3 layers

Results and discussion

Studies of the ice-forming activity of the prepared reagents were carried out at CAO under the standard "Laboratory Method for Evaluating the Efficiency of Ice-Forming Reagents and Pyrotechnic Compositions in Laboratory Conditions" [18].

The yield of active particles per gram of preparation in a laboratory cloud chamber at temperatures of supercooled fog from -3 ºC to -12 °C, the moisture absorption capacity of the preparations, the size distribution and shape of the resulting particles were determined during testing.

The aerosol was obtained by spraying 10-20 mg of the reagent powder from a small glass using a syringe, followed by injection (insufflation) of the sample into a separate 800-liter aerosol chamber. After mixing and leveling the concentration with a fan, a sample of the obtained aerosol in optimum volume (from 20 to 150 cm^3 at different fog temperatures) was introduced into a supercooled fog into a cloud chamber (300 liters volume). The formed ice crystals were registered by the replica method.

Table 3 [19,20] gives generalized data on the yield of active particles for the investigated AgI-containing crystallizing reagents and pure silver iodide obtained using a two-stage CAO generator. For comparison, the average yields of active particles for the currently used pyrotechnic composition AD-1 containing 8% AgI are shown.

As can be seen from Table 3, the yield of active particles for reagents based on nanoscale silica is higher than that for pyrocomposition AD-1 with the advantage of nanoscale preparations being particularly high at a limit temperature of -3 °C.

Table 3

Temperature dependences of the yield of active particles on preparations based on silver iodide and pure AgI

Temperature, °C	AgI		Pyrotechnic composition AD-1
	Pure substance	On nanosilica surface	
-12	$(5 \div 7) \cdot 10^{14}$	$(5 \div 40) \cdot 10^{13}$	$(1 \div 2) \cdot 10^{13}$
-10	$(2 \div 4) \cdot 10^{14}$	$(2 \div 40) \cdot 10^{13}$	10^{13}
-8	$(2 \div 3) \cdot 10^{13}$	$(2 \div 20) \cdot 10^{13}$	$(5 \div 7) \cdot 10^{12}$
-6	$(2 \div 4) \cdot 10^{12}$	$(4 \div 40) \cdot 10^{12}$	$(2 \div 4) \cdot 10^{12}$
-5	$5 \cdot 10^{11}$	$(2 \div 7) \cdot 10^{12}$	10^{12}
-4	limit of action	$(2 \div 20) \cdot 10^{11}$	$(5 \div 7) \cdot 10^{11}$
-3	–	$10^{11} \div 10^{12}$	$(3 \div 6) \cdot 10^{10}$

Table 4 shows the temperature dependences of the yield of active particles for the most effective samples M-333 and LN-212 studied. For comparison, the efficiency values for the pyrotechnic composition of AD-1 tested at CAO in 2013 are given. At the temperature of supercooled fog of -10 °C, the yield of active particles for the most effective preparation LN-212 was $4 \cdot 10^{14}$ per 1 g of composition, and at temperature of –3 ÷ –5°C it was $(1 \div 8) \cdot 10^{12}$.

Table 4

Comparison of the temperature dependences of the yield of active particles for the most effective preparations with AgI

Temperature, °C	M-333	LN-212	AD-1
-12	$5.50 \cdot 10^{13}$	$5.0 \cdot 10^{14}$	$1.27 \cdot 10^{13}$
-10	$4.60 \cdot 10^{13}$	$5.0 \cdot 10^{14}$	$1.23 \cdot 10^{13}$
-8	$1.53 \cdot 10^{13}$	$3.50 \cdot 10^{14}$	$7.84 \cdot 10^{12}$
-6	$8.0 \cdot 10^{12}$	$4.40 \cdot 10^{13}$	$2.84 \cdot 10^{12}$
-5	$6.0 \cdot 10^{12}$	$8.0 \cdot 10^{12}$	$1.0 \cdot 10^{12}$
-4	$1.08 \cdot 10^{12}$	$2.80 \cdot 10^{12}$	$3.52 \cdot 10^{11}$
-3	$9.66 \cdot 10^{11}$	$\sim 10^{12}$	$6.0 \cdot 10^{10}$

The tests showed that the ice-forming activity per mass unit of the AgI substance and phloroglucinol deposited on the surface of silica nanoparticles according to the GSSAM technology corresponds to the values of native preparations. In this case, the best sample containing AgI (Fig. 3) is superior in efficiency to the known AD-1 reagent.

Fig. 3. Photo of AgI/nanosilica powdery reagent (LN-212).

Conclusions

The results of the research have proved that the use of nanoscale highly disperse silica carrier and GSSAM technology of its modification with active ice-forming substances allows obtaining effective powder reagents for weather modification based on the principle of Levilites.

Such powder highly disperse nanoscale reagents have a number of advantages over the currently used pyrotechnic flares and burning of solutions:

- GSSAM technology allows creating a uniform layered coating or clusters on a surface of silica nanoparticles with practically any ice-forming substances such as organic, e.g., phloroglucinol, 1,5-dioxinaphthalene, copper acetylacetonate, and inorganic salts, e.g., metal iodides and chlorides and ammonium. Choosing the nature of the active substance, one could create both crystallizing and hygroscopic reagents.
- It is technically possible to combine several different active substances of different nature in an ice-forming preparation. This circumstance opens the possibility to create new reagents optimized by various parameters such as efficiency, price, availability of components, environmental friendliness, etc.
- When pyrotechnic flares and burning of solutions are used, the formation of highly disperse particles (nuclei of ice formation) takes place when a reagent is introduced into the zone of action. As noted, several factors influence this process that is difficult to predict. In our case, the reagent already contains the ice nuclei formed during the synthesis process. Their number and parameters, if necessary, can be estimated in advance.
- The process of introducing the reagent into the impact zone is greatly simplified. For this purpose it is sufficient to spray powder agent due to the air flow.

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ნანოზომის კაჟბადის ოქსიდის საფუძველზე დამზადებული ყინულწარმომქმნელი ფხვნილისებური რეაგენტების თვისებები და უპირატესობები

ე. ვორონინი, ლ. ნოსაჩი, ვ. გუნკო, ე. სოსნიკოვა,
ბ. დანელიანი, ბ. ხარმასი

რეზიუმე

მაღალდისპერსული ნანოზომის კაჟბადის ოქსიდის (SiO_2 (IV)) ვერცხლის იოდიდით და ფლოროგლუცინით აირფაზური სოლვატო-სტიმულირებული ადსორბციული მოდიფიცირების (ასსამ) გზით იქნა სინტეზირებული ლევილიტების პრინციპზე დაფუძვნებული რიგი ყინულწარმომქმნელი რეაგენტები ფხვნილის სახით. მიღებული რეაგენტების ლაბორატორულმა კვლევებმა გვაჩვენა, რომ (ასსამ) ტექნოლოგიით მაღალდისპერსული ნანოზომის კაჟბადის ოქსიდის ზედაპირზე დატანილი AgI და ფლოროგლუცინის ნივთიერების ყინულწარმომქმნელი აქტიურობა მასის ერთეულზე ნატიური პრეპარატების მნიშვნელობებს შეესაბამება. ამასთანავე AgI-ს შემცველი საუკეთესო ნიმუში თავის ეფექტურობით აღემატება ცნობილ АД-1 ტიპის რეაგენტს.

Свойства и преимущества порошковых льдообразующих реагентов на основе наноразмерного кремнезёма

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Резюме

Путём газофазного сольвато-стимулированного адсорбционного модифицирования (ГССАМ) высокодисперсного наноразмерного кремнезёма иодидом серебра и флороглюцином был синтезирован ряд порошковых льдообразующих реагентов, основаных на принципе левилитов. Лабораторные исследования полученных реагентов показали, что льдообразующая активность на единицу массы вещества AgI, и флороглюцина, нанесённых на поверхность наночастиц кремнезёма по ГССАМ-технологии, соответствует значениям нативных препаратов. При этом лучший из образцов, содержащий AgI, превосходит по эффективности известный реагент АД-1.