Cryogelation of individual and complex nanooxides under different conditions

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GRAPHICAL ABSTRACT
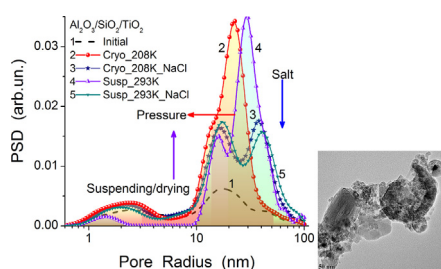
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ABSTRACT

To study changes in the characteristics of gelled/dried nanooxides (fumed silicas PS300 and PS100, alumina, silica/titania ST, alumina/silica/titania AST), high-pressure cryogelation, HPCG (at 208 K or 260 K) or gelation (293 K, 1 atm) was carried out using 20 wt.% aqueous suspensions pure or with addition of 0.1 M NaCl. The nanooxide samples were studied after drying at room temperature. Maximal changes in the textural and crystalline characteristics are observed for cryogels with AST prepared at ∼1000 atm and 208 K due to decomposition of complex nanoparticles. Its specific surface area S_{BET} increases from 83 to 160 m^2/g, and the crystallinity degree grows by 11%. Mixing of PS300 and AST (1:1, w/w) in the suspension prevents the decomposition of AST particles in the cryogel since S_{BET} decreases in comparison with that of the initial blend powders. Addition of NaCl (2.8 wt.% in dried powders) reduces decomposition of AST particles due to changes in HPCG conditions. For binary ST, S_{BET} increases but much smaller than for AST. HPCG of individual silica and alumina leads to a decrease in the S_{BET} value; *i.e.* nanoparticles are not decomposed. A significant increase in the volume of large mesopores (pore radius 5–10 nm < R < 25 nm) and macropores (25 nm < R < 60–100 nm) is observed for gelled/dried samples in comparison with the initial powders. Contribution of nanopores (R < 1 nm) and narrow mesopores (1 nm < R < 5–10 nm) decreases after HPCG. The effects of NaCl and HPCG on the textural characteristics are minimal for ST studied.

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1. Introduction

Fumed oxides are important materials for a variety of industrial, medical and other applications. Their annual production (mainly fumed titania and silica) in the world is greater than 10^7 tonnes.

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These materials synthesised with metal chlorides or other (*e.g.* organometallics) precursors at high temperatures in the $O_2/H_2/N_2$ flame [1–3] are named "nanooxides" because they are composed of nanosized primary particles. For instance, ultra-fine nanosilica at high specific surface area $S_{BET} \approx 500\ m^2/g$ has the average diameter of nanoparticles $d_{av} \approx 5.5\ nm$, much larger $d_{av} \approx 55\ nm$ is for A–50 or Degussa OX–50 and $d_{av} \approx 100\ nm$ for disperse silica at $S_{BET} \approx 30\ m^2/g$ [4–6]. Fumed oxides with titania, alumina, *etc.* are composed of smaller primary particles than nanosilica with the same specific surface area. This is due to their greater true density, *e.g.* fumed anatase at $S_{BET} \approx 50\ m^2/g$ has $d_{av} \approx 31\ nm$ which is smaller than that of OX–50 or A–50 ($\sim$55 nm) with similar S_{BET} value. Complex fumed nanooxides such as silica/titania or silica/alumina are composed of nanoparticles similar to those of individual oxides but they include different oxide phases and mixed fragments. Thus, the diameters of spherical-like nonporous primary particles of nanooxides can be mainly in the 5–100 nm range [1–8]. This morphological feature is of importance for practically all properties of fumed oxides and, therefore, for their numerous applications.

One of important structural features of fumed nanooxides is the absence of valence bonding of primary nanoparticles in their aggregates and agglomerates of aggregates [1–8]. This bonding is mainly due to electrostatic and dispersion forces and hydrogen bonds between surface hydroxyls of adjacent nanoparticles. Adsorbed water located in contact zones of adjacent nanoparticles can play a certain role in this bonding [4]. The nanooxide powders are rather "soft" matters of a low bulk density ρ_b (*e.g.* 0.04–0.13 g/cm^3 for different nanosilicas) and a small amount of water (0.5–3 wt.% for nanosilicas) adsorbed from air [9,10]. Some treatments (such as hydrothermal, thermal, chemical modification of a surface with cross-linking of modifiers) of nanooxides [1–4] can lead to formation of chemical bonds between adjacent nanoparticles. Surface hydroxyls play an important role in this bonding, as well as in many other properties of nanooxides [1–10]. Another problem related to changes in the morphology of nanoparticles *per se* during different treatments is less studied than effects of surface modification of nanoparticles [1–11]. Investigations of the influence of different treatments of nanooxides on the morphology of nanoparticles and the properties of whole materials are of importance from both theoretical and practical points of view. Notice that nanooxides can be used in the form of aqueous suspensions pure or with 0.1 M NaCl as medicinal preparations [6]. Therefore, the NaCl effects on the behaviour of nanooxides in initial and frozen suspensions are of interest for practical applications. For instance, pure aqueous suspensions of nanosilica frozen and then thawed lose the aggregative stability and cannot be completely re-suspended.

Previously [11], high-pressure cryogelation (HPCG) of nanosilica was studied using concentrated aqueous suspensions (5–20 wt.%) at low temperature ($\sim$260 K) and high pressures (450–1000 atm) in comparison with the initial powder and suspended-dried samples prepared under standard conditions. During HPCG, ice crystallites playing a role of porogens [12] can produce very high pressure in restricted volume (up to 2000 atm in a container with absolutely rigid walls and $\sim$1050 atm in a freezing bomb with stainless steel) [13]. Obtained results [11] showed changes in the textural and adsorption characteristics of nanosilica depending on its concentration in the suspensions and HPCG conditions. Composition of nanoparticles of complex oxides can affect results of HPCG and the properties of final cryogels due to the differences in the pressure and temperature behaviours of different phases in complex nanoparticles. This reason is a 'driving force' of the present investigation of HPCG of complex nanooxides in comparison with individual ones.

Cryogels with inorganic materials (including silica, alumina, titania), as well as gels, can be synthesised using low-molecular weight compounds (*e.g.* tetraethyl orthosilicate, titanium tetraisopropoxide, metal chlorides) or high-molecular weight compounds [12–35]. Oxide nanoparticles can be considered as analogues of polymers used in cryogelation with cross-linking of macromolecules [12]. The textural and morphological characteristics of inorganic cryogels can be varied depending on water content (since ice crystallites play a role of a porogen templating pores), precursor types, time, temperature, temperature gradient, and other conditions [12–35]. During preparation, some inorganic cryogels were frozen at very low temperatures (77.4 K) [14–17]; however, higher temperatures (between $-12\,^{\circ}C$ and $-20\,^{\circ}C$) are typically used in cryogelation. Despite numerous papers published on inorganic gels and cryogels (see, *e.g.* [12–35] and references in them), there are no cryogels studied with complex oxides or different nanosilicas prepared at low temperatures and very high pressures ($\sim$1000 atm) in cryo-bombs. Therefore, the aim of this paper is to study the high-pressure cryogelation effects for fumed oxides: nanosilicas PS300 and PS100, nanoalumina, silica/titania, and alumina/silica/titania using aqueous suspensions without and with addition of NaCl (0.1 M) prepared at very high pressures ($\sim$1000 atm) in high-pressure stainless steel reactors (freezing bombs, cryo-bombs) at 208 K or 260 K in comparison with the initial powders and the products of gelation of the same nanooxides at standard conditions (293 K, 1 atm). It should be noted that nanooxides are very appropriate precursors for preparation of inorganic cryogels due to features of their particulate morphology (nanosized particles weakly aggregated in loose aggregates and very loose agglomerates of aggregates), texture (high specific surface area, low bulk density) and ease rearrangement of nanoparticles in fumed oxides under external actions due to weak bonding of nanoparticles in secondary structures that is of importance to control the characteristics of cryogels.

2. Materials and methods

2.1. Materials

Individual oxides: **p**yrogenic (fumed) **s**ilicas PS300 and PS100 (S_{BET} = 302 and 84 m^2/g, respectively) and fumed alumina (S_{BET} = 89 m^2/g), fumed silica/titania ST (20 wt.% of titania, S_{BET} = 87 m^2/g) and fumed alumina/silica/titania AST (89 wt.% of partially crystalline alumina, 10 wt.% of amorphous silica, and 1 wt.% of titania as a small number of titania nanoparticles doped by silica and alumina and a solid solution of titania in alumina and silica phases, S_{BET} = 83 m^2/g) were used as the initial powder materials (pilot plant of the Chuiko Institute of Surface Chemistry, Kalush, Ukraine). Binary and ternary fumed oxides were prepared by simultaneous high-temperature hydrolysis of the corresponding metal chlorides ($SiCl_4$, $AlCl_3$, $TiCl_4$). The initial nanooxide materials were described in details elsewhere [4,5,36,37]. Notice that four materials from five ones having close S_{BET} values (83–89 m^2/g) were selected for more clear analysis of the effects of the chemical composition of nanooxides on the cryogelation results. Two fumed silicas PS300 and PS100 were selected to analyse the influence of the specific surface area on the characteristics of the cryogels.

Aqueous suspensions of nanooxides (20 wt.%) were prepared using doubly distilled water or 0.1 M NaCl solution sonicated (22 kHz) for 5 min. The dispersions were then frozen at 260 K (for 12 or 24 h) or 208 K (for 12 h) in thick-walled stainless steel reactors at pressures of up to 1050 atm, caused by ice crystallites formed in the frozen suspensions ($\sim$10–15 mL) placed in strongly restricted volume of the cryo-bombs. The pressure of ice ($\sim$1000 atm) in the cryo-bombs was estimated according to the literature [13,38,39]. Then cryonanooxide (CNO) samples were dried in glass dishes in air at room temperature for 2–5 days to air-dry state. The same