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Control of the growth processes of the silica sols colloidal particles

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Abstract

Solubility of the silica depends mainly on medium pH values. Owing to this pH factor becomes definitive when carrying processes connected with the silica dissolving. The growth of the silica colloidal particles during the obtaining stabilized silica sols is one of such processes. The influence of other factors on the silica solubility in the SiO_2–H_2O system is not so essential.

A possibility to control the growth of the silica colloidal particles during the preparation of the stabilized silica sols by means of regulating medium pH values has been studied. Seed formation processes are decisive when obtaining silica sols and silica gels with beforehand requested characteristics. It is necessary to realize growth processes in the meta-stable range of the SiO_2–H_2O system (pH 8.5–9.5) to obtain silica sols with reproducible particle sizes.

Influence of the pre-history of obtained stabilized silica sols on porous characteristics of silica gels prepared on their base has been studied. For evaluation of the quality of these sols porous characteristics of the silica gels have been determined by means of BET method. Pore size distribution has been also determined for the obtained silica gels.

Keywords: Seed formation; Colloidal particles' growth; Silica; Pore size distribution; BET method

1. Introduction

Despite the fact that colloidal silica as investigation object was studied for many years the interest towards this system does not only weaken but on the contrary becomes stronger. Particularly in the recent years with appearing of the nanotechnology during the preparation of materials on the base of silica the role of the colloidal silica as well as the problems of its stabilization increases [1–7].

Synthesis of highly transparent hybrid films containing nanosized silica domain from acrylic polymer and aqueous monodispersed colloidal silica with a coupling agent 3-(trimethyloxysilyl)propyl methacrylate (MSMA) was described in [1,2]. The silica content in the hybrid thin films was varied from 0 to 50wt.%. The experimental results showed that the silica particle size in the precursor solution and the hybrid films was varied from 20 to 40nm. It could be controlled by the mole ratio of MSMA to silica.

Preparation and thermal properties of epoxy-silica nanocomposites from nanoscale colloidal silica was discussed in [3]. Nanocomposites were obtained from directly blending diglycidylether of bis-phenol-A and nanoscale colloidal silica and then curing 4,4-diaminophenylmethane.

Properties of poly(*N*-isopropylacrilamide)-grafted colloidal silica were studied in [4]. Poly(*N*-isopropylacrilamide-co-3-trimethoxysilylpropylmethacrylate) was prepared by radical polymerization and was grafted onto the surface of spherical colloidal silica. The copolymer, which had on average one silyl group per chain, condensed on the silica dispersed in tetrahydrofuran at 60 °C.

The influence of cationic polyelectrolytes on the stability and flocculation of dispersed particles, the poly-

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mer adsorption on colloidal silica and quartz powder was investigated in [5].

Preparation and characterization of polypyrrole–silica colloidal nanocomposites in water–methanol mixtures was discussed in [6]. The effect of methanol cosolvent on the synthesis of polypyrrole–silica colloidal nanocomposites using ultra fine silica sols in combination with both iron(III) chloride and oxidants has been investigated. Two protocols were valuated: the addition of methanol to an aqueous silica sol and the addition of water to methanolic silica sol. The latter proved to be more robust, since it allowed colloidally stable dispersions to be prepared at higher methanol content. This allowed greater control over the particle size of the nanocomposites particles.

Surface chemistry and trimethylsilyl functionalization of Stöber silica sols were investigated in [7]. Various silica sols, with different surface chemistries, were reacted in solvent dispersions with hexamethyldisilazane or ethoxytrimethylsilane to produce hydrophobic trimethylsilane trimethylsilyl functionalized sols.

Manufacturing of silica sorbents for liquid chromatography, especially high performance liquid chromatography (HPLC) is one more important area in which colloidal silica is used. Total control of the whole technological processes is necessary to provide manufacturing the packing materials for HPLC with reproducible physical–chemical properties [8,9]. One of the ways to secure the control of porous characteristics of the silica sorbents is the using of stabilized silicas as initial raw materials. Recently works dedicated to the obtaining and stabilization of colloidal silica were appeared [10–12].

Influence of the process parameters on the morphological evolution and fractal dimension of sol-gel colloidal silica particles have been studied in [10]. Colloidal silica particles were synthesized from tetraethoxysilane (TEOS), ammonium hydroxide, ethanol, and deionized water. Obtaining different structures was possible due to the variation of molar ratios of ammonium hydroxide, ethanol and water with respect to the precursor. Pore structure was characterized by nitrogen gas sorption–desorption, showing colloidal silica particles with solid-pores surface areas varying from 0.48 up to 567 m^2/g, pore volume varying from 0.0013 up to 0.88 cm^3/g, and average pore radii varying between 14 and 36 nm.

The process parameters of the formation colloidal silica via sodium silicate have been investigated in [11]. Sodium ion of delicate was removed by ion-exchanging to obtain the active silicic acid which was titrated to the solution of potassium hydroxide to form the colloidal silica. The results showed the mean particles size of colloidal silica was influenced by the KOH concentration, formation temperature and low titration rate of active silicic acid would help the particle growth to form the larger particle size of colloidal silica. Unfortunately, the colloidal silicas formed at theses conditions were unstable.

Preparation of colloidal silica from sodium metasilicate solution and sulfuric acid in emulsion medium was described in [12]. The problem of the synthesis of the silica sols with colloidal particles of definite fixed sizes is very important during the process of obtaining silica gels with reproducible porous characteristics on the base of stabilized silica sols. Control of the particles' growth processes is necessary in this case in order to secure reproducibility of the porous characteristics of the obtained silica sols.

The obtaining of silica gels on the base of stabilized silica sols has the following advantages as compared with the classical method for obtaining silica gels by means of the precipitation by acids from the liquid glass:

- possibility of the control of the porous characteristics of the obtained silica gels;
- reproducibility of the porous characteristics;
- the absence of the necessity of the silica hydrogels rinsing [8].

Medium acidity (pH-factor) is the main, and it can be said decisive factor during the carrying processes in the SiO_2–H_2O system so far as solubility of the silica depends on the highest level from the medium pH values. The growth of the silica colloidal particles during the obtaining of the stabilized silicas is one of such processes.

Series of methods for obtaining silica sols was described [13–15]. Method of Bechtold–Snyders [14] is most frequently used in which silica sols with particles 10–130 nm in size are usually obtained regulating colloidal particles' growth processes. Colloidal particles' growth process is provided by adding the "active silica" (silica sol with particles diameter less than 2–4 nm) to the "main" silica. Preparation of the "active silica" is realized by passing the sodium silicate solution with silicate module $M = 3.25$ ($M = SiO_2/Na_2O$ molar ratio) through the ion-exchange columns in H^+-form after which pH value of the solution rises up to 7.0. The main silica sol is prepared by heating the part of "active silica" up to 100 °C when colloidal particles more than 10 nm in size are formed as a result. Grafting is carried by heating the system at the temperatures lower than 60 °C maintaining volume constant (that is the rate of adding "active silica" must be equal to the rate of water removing from the system owing to evaporation).

Seed formation (nucleation) processes in this case occurs spontaneously. As a point of fact, the silicon dioxide colloidal particles' growth takes place on the centers already formed by the non-regulated, fortuitous way. At pH 7.0 also new seeds appear side by side with growth of