PHYSICS AND CHEMISTRY
OF SOLID STATE
V. 22, No. 4 (2021) pp. 724-728

Section: Chemistry

DOI: 10.15330/pcss.22.4.724-728

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ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 22, № 4 (2021) С. 724-728

Хімічні науки

UDC: 544.723 ISSN 1729-4428

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Gas-phase crosslinking of the lignin on the nanoscale fumed silica surface

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A method for the polymerization modification of nanoscale fumed silica by crosslinking a lignin layer adsorbed on a nanosilica surface under a gas dispersion medium is described. A mixture of phenol and formaldehyde in the presence of HCl proved to be the most effective crosslinking agent. It has been suggested that the crosslinking of lignin molecules occurs by a mechanism similar to the production of phenol-formaldehyde resins.

Keywords: fumed nanosilica, lignin, polymerization modification, adsorption modification, mechanical treatment, gas-phase crosslinking.

Received 15 August 2021; Accepted 15 November 2021.

Introduction

Amorphous non-porous highly disperse nanoscale silica (nanosilica) is the first industrial product of nanotechnology [1]. At the Chuiko Institute of Surface Chemistry NAS of Ukraine in the1980s the effective sorption-detoxifying drugs "Silics", "Sillard" and "Polysorb MP" based on nanosilica were developed and introduced into medical practice [2-9]. Currently, nanosilica is the initial substance for enterosorbents produced in Ukraine and Russia under the commercial names "Silics", "Sillard", "White Coal", "Atoxil" and "Polysorb MP" [8-12].

Such nanosilica has S_{BET} = 300 m^2/g and consists of spherical particles with a diameter of ~ 10 nm. If a layer of biologically active substance (BAS) is applied to the surface of nanosilica particles, and then an additional polymer layer is formed, a nanosized capsule of the core-shell type will be obtained (Fig. 1). The rate of BAS release from such nanocapsule will be largely determined by the structure of the polymer shell.

Thus, in order to create new promising combined preparations with a wide spectrum of actions based on nanosilica, it is important to purposefully form the layers of BAS and polymer on its surface.

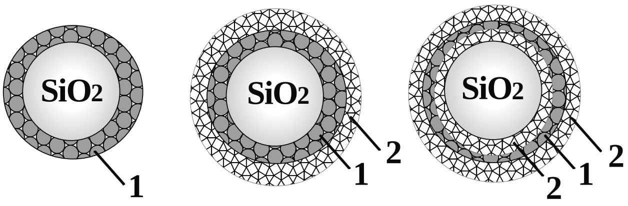

Fig. 1. Schematic representation of core-shell nanocapsules based on nanosilica: 1 - BAS, 2 - polymer.

This process is called as fumed silica modification with non-volatile organic compounds. All types of modification methods are divided on gas-phase and liquid-phase according to the physical state of the dispersion medium where the process takes place [13, 14]. Each method has its advantages and disadvantages. However, to create a real (non-laboratory) technology for modifying highly dispersed silica, the liquid-phase method is unacceptable.

As a result of many years research the laboratory and pilot technologies for the adsorption modification of fumed silica with non-volatile organic compounds and polymers under the conditions of a gas dispersion medium were developed in Chuiko Institute of Surface Chemistry of NAS of Ukraine [15-23].

The aim of this work was to test the applicability of this technology for the polymerization modification of fumed silica in a gas dispersion medium. Adsorption modification of fumed silica is a one-step process and consists in applying non-volatile substances onto the surface as a result of migration in a specially selected atmosphere. Polymerization modification is more complicated and contains two stages: 1) adsorption modification with oligomers and 2) bonding of sorbed oligomer molecules by reaction with crosslinking agents and the formation of insoluble crosslinked polymers [13, 14, 24, 25].

I. Materials and methods

Fumed silica A-300 (Pilot plant at the Institute of Surface Chemistry, Kalush, Ukraine) was used as the initial material. Lignin (Lignosulphonate DP-1962, Borregaard Company, Sarpsborg, Norway) was used as a modifier.

Lignin is a complex three-dimensional network polymer having an aromatic nature [26]. The lignin molecule is large with an indefinite composition and has many diverse functional groups. The main functional groups of lignin are methoxyl, alcohol and phenolic hydroxyl groups, as well as carbonyl and carboxyl groups.

According to the literature, lignin can be an excellent object for chemical modifications due to its highly functional nature. The review [27] describes in detail various chemical modifications of lignins. They are divided into three groups: 1) lignin fragmentation into phenolic or other aromatic compounds, 2) synthesis of new chemical active centers, and 3) functionalization of hydroxyl groups to increase their reactivity. For lignin, such reactions are characteristic - hydrogenation, hydrolysis, oxidation, pyrolysis, halogenation, nitration, amination, alkylation, and others [28-30]. However, almost all of these reactions, with the possible exception of pyrolysis, occur in various solvents or water. This makes them unsuitable for solving our problem - to realize a gas-phase crosslinking of a layer of lignin adsorbed on the fumed silica surface.

In this study, we tested the following binders: glutaraldehyde, formaldehyde, polyethylene glycol, polyvinyl alcohol, phenol (China). Aqueous solutions of NH_3 and HCl were used as a catalyst.

Modification was carried out in a ball mill. A study of two types of modification was carried out - adsorption and polymerization.

For adsorption modification, fumed silica, lignin in an amount of 200 mg/g (monolayer) and a small amount of water (400 mg per 1 g of SiO_2) were loaded into a ball mill. Earlier, we showed that in this case fumed silica completely retains its flowability [20-23]. The mechanical treatment time was 2 hours. Then the sample was unloaded and heated at 85 °C to remove solvent vapor.

For polymerization modification fumed silica, lignin in an amount of 200 mg/g (monolayer), a binder (or a mixture thereof) and a catalyst were successively loaded into the ball mill. The total amount of water in the reaction mixture was 400 mg per 1 g of SiO_2. The mechanochemical treatment time was 2 hours. Then the sample was unloaded and heated at various temperatures in the range from 85 to 200 °C.

IR spectra of modified fumed silica were recorded on a Specord M80 spectrophotometer (Germany) in the range of 1200-4000 cm^{-1}.

An express analysis of the result of the crosslinking process was carried out by changing the color of the solution over the precipitate of an aqueous suspension of modified fumed silica. 5% (wt.) aqueous suspensions of the obtained samples were prepared. The lignin aqueous solution has a brown color and contains absorption bands with maxima of ~ 220 and 270 nm in the electronic spectrum. The lignin concentration in the equilibrium solutions of the studied samples was determined on a Specord M40 instrument (Germany).

II. Results and discussion

Adsorption modification of fumed silica with lignin.

The main active sites of the fumed silica surface are the isolated silanol groups ≡Si-OH, which in the IR spectrum appear as an intensive narrow absorption band (ν_{OH}) with a maximum of 3750 cm^{-1} (Fig. 2, line 1). The concentration of free silanol groups on the surface of the used nanosilica is 0.8 mmol/g. Adsorption interaction with organic molecules that have polar functional groups occurs as a result of the formation of hydrogen bonds with silanol groups. In this case, the ν_{OH} value of the perturbed silanol groups decreases, and the band maximum shifts toward longer waves. The degree of perturbation of the ≡Si-OH groups characterizes the degree of surface coverage (Θ), which can be calculated from the ratios of the optical densities of the 3750 cm^{-1} band before and after adsorption (D_0 and D, respectively) by the formula:

$$\Theta = 1 - D/D_0$$

where D and $D_0 = \log T_0/T$;

and T_0 and T are the transmission of infrared radiation in the baseline and at the maximum of the band.

The IR spectra of modified silicas and the indicated dependences are shown on Fig. 2 and 3. Previously, we found [21] for linear macromolecules of polyoxyethylene and polyvinylpyrrolidone that when the polymer content on the surface of fumed silica is approximately 200 mg/g, all silanol groups are perturbed. As can be seen from fig. 3, in this case, the degree of perturbation was only about 40%. We believe that this is due to the three-dimensional structure of the lignin molecule. This means that most of the functional groups of the adsorbed molecules are free to implement the crosslinking process on the surface of fumed silica.

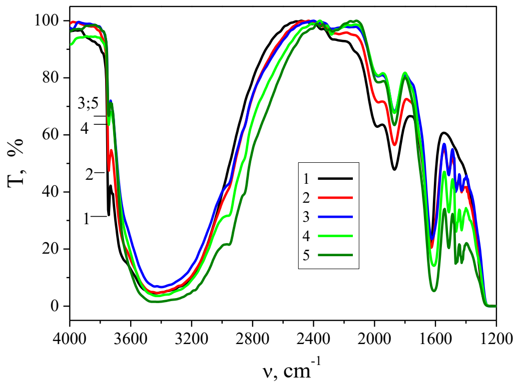

Fig. 2. IR spectra of fumed silica: 1 - initial, 2-5 - containing 50, 100, 150 and 200 mg/g of lignin, respectively.

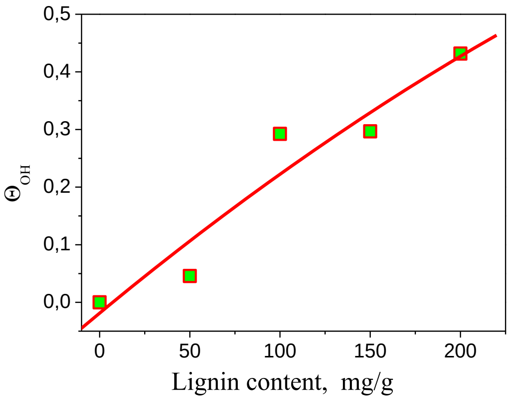

Fig. 3. Dependence of the degree of perturbation of surface silanol groups of fumed silica on the lignin content

Polymerization modification of fumed silica with lignin.

12 samples that had different combinations of silica, binder and catalyst were prepared and analysed. The degree of crosslinking was determined by the amount of lignin that was desorbed from the surface of fumed silica after its contact with water. Polymerized lignin is insoluble, so it should not be desorbed. The lignin content in the equilibrium solution was determined by UV Vis spectroscopy.

The best result was observed for the sample where a mixture of phenol and formaldehyde with HCl as a catalyst were used. On Fig. 4 shows photographs of silica-lignin nanocomposites - the initial sample (1.01) and the sample after crosslinking (1.02).

5% (wt.) aqueous suspensions were prepared from these samples. After 30 minutes of contact, the suspensions were centrifuged and UV Vis spectra equilibrium solutions (diluted) were obtained (Fig. 5).

Lignin concentrations in equilibrium solutions were calculated. They amounted to: initial sample 1.01 (control) - 28 mg/ml, crosslinked sample 1.02 - 4.5 mg/ml, i.e. 6.1 times lower. This means that approximately 84% of the lignin on the surface of the silica is polymerized.

Fig. 4. Fumed silica modified by lignin before (sample 1.01) and after (sample 1.02) crosslinking.

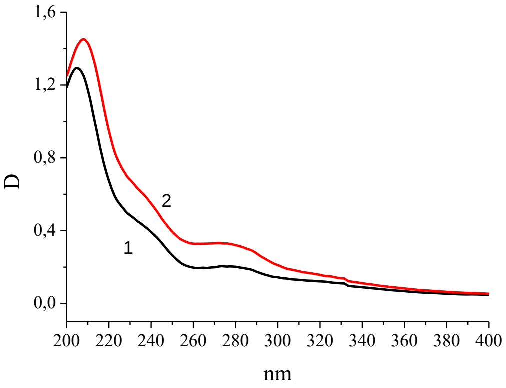

Fig. 5. UV Vis spectra of equilibrium solutions: 1 - sample 1.01 (dilution 21 times); 2 - sample 1.02 (dilution 200 times).

It has been suggested that the lignin molecules are crosslinked according to a mechanism similar to the production of phenol formaldehyde resins [31] where aromatic units of lignin reacts with formaldehyde at the ortho sites (sites 2 and 6) allowing up to 2 units of formaldehyde to attach to the ring (Fig.6).

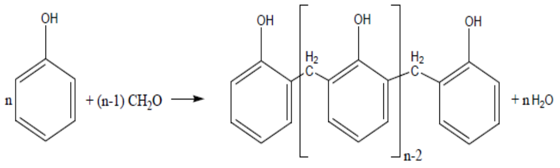

Fig.6. Schema of the production of phenol formaldehyde resins.

The initial reaction in all cases involves the formation of a hydroxymethyl phenol, which is capable of reacting with either another free site in aromatic unit of lignin, or with another hydroxymethyl group. The first reaction gives a methylene bridge, and the second forms an ether bridge: As a result, branched lignin molecules are crosslinked through a methylene bridge and an ether bridge.

Such an assumption requires further investigation.

Conclusions

A method for crosslinking a lignin layer adsorbed on a nanoscale fumed silica surface under a gas dispersion medium has been developed. A mixture of phenol and formaldehyde in the presence of HCl proved to be the most effective binding agent.

Acknowledgement

This publication is part of the research work at KTH - Royal Institute of Technology, Stockholm, Sweden, funded by a Swedish Institute scholarship

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Газофазне зшивання лігніну на поверхні нанорозмірного високодисперсного кремнезему

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Описано спосіб полімеризаційного модифікування нанорозмірного діоксиду кремнію шляхом зшивання шару лігніну, адсорбованого на поверхні нанокремнезему в умовах газового дисперсійного середовища. Суміш фенолу та формальдегіду в присутності HCl виявилася найефективнішим реагентом для зшивання молекул лігніну. Висловлено припущення, що зшивання молекул лігніну відбувається за механізмом, подібним до отримання фенолформальдегідних смол.

Ключові слова: високодисперсний нанорозмірний кремнезем, лігнін, полімеризаційне модифікування, адсорбційне модифікування, механічна обробка, газофазне зшивання.