Inorganica Chimica Acta 362 (2009) 2222–2230

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Formation of the nanostructure on a silica surface as mercury(II) ions adsorption sites

Lyudmila Alekseevna Belyakova, Oleksandra Mikolaevna Shvets *, Diana Yur'evna Lyashenko

Chuiko Institute of Surface Chemistry, National Academy of Sciences of Ukraine, General Naumov str. 17, Kiev 03164, Ukraine

ARTICLE INFO

Article history:
Received 13 June 2008
Received in revised form 8 October 2008
Accepted 14 October 2008
Available online 22 October 2008

Keywords:
Silica surface
β-Cyclodextrin
Immobilization
Adsorption
Mercury(II)
Inclusion complex

ABSTRACT

The present work investigates the adsorptive interactions of Hg(II) ions with hydroxylated silica, aminopropylsilica and silica chemically modified by β-cyclodextrin in aqueous medium. Batch adsorption studies were carried out with various agitation time and mercury(II) concentration. The maximum adsorption was observed within 15–30 min of agitation. The kinetics of the interactions, tested with model of Lagergren for pseudo-first and pseudo-second order equations, showed better agreement with first order kinetics ($k_1 = 3.4 \pm 0.2$ to 5.9 ± 0.3 min^{-1}). The adsorption data gave good fits with Langmuir isotherms. The results have shown that β-cyclodextrin-containing adsorbent has the largest adsorption specificity to Hg(II) : $K_L = 14400 \pm 700$ L/mg. "β-Cyclodextrin–NO_3^-" inclusion complexes with ratio 1:1 and super molecules with composition $C_{42}H_{70}O_{35} \cdot 3Hg(NO_3)_2$ are formed on the surface of β-cyclodextrin-containing silica.

1. Introduction

Cyclodextrins are cyclic oligomers of α-D-glucose. They are widely used for enhancement of solubility and stability of medicines and bioactive compounds due to their unique ability to form inclusion complexes of the "host–guest" type [1,2]. Cyclodextrins also are promising for creation of selective adsorbents, active catalysts and sensors [3–5], chromatographic separation and purification of organic compounds of similar structure and composition [6], extracting and concentrating of impurities of toxic substances [7]; creation of medicines with prolonged action, and decreasing of toxicity of medicines [8,9].

Of great importance is the investigation of adsorption specificity toward heavy metals ions for their chemical analysis, removal of polluting species from wastewater and its utilization [10–12]. Insoluble cyclodextrins and cyclodextrins immobilized on a different supports including inorganic carriers are the most suitable for practical purposes [1,2,13].

In the present work the influence of chemical immobilization of β-cyclodextrin on adsorption ability of amorphous mesoporous silica to Hg(II) ions has been studied.

2. Experimental

2.1. Materials

The mesoporous amorphous silica – Silochrome C-120 with the specific surface area of 118 m^2/g, average pore diameter of 40 nm, and silanol groups concentration of 0.4 mmol/g was used as starting silica adsorbent and support for synthesis of organosilicas.

β-Cyclodextrin (β-CD, Fluka), 4-toluenesulfonyl chloride (tosyl chloride, TsCl, Merck) and mercury(II) nitrate ($Hg(NO_3)_2 \cdot H_2O$, Khimlaborreaktiv) were used without additional purification.

2.2. Methods

Infrared transmission spectra of pressed plates (10–15 mg/cm^2 under pressure 10^8 Pa) were recorded over the spectral range 4000–400 cm^{-1} using a Thermo Nicolet NEXUS FT-IR spectrophotometer.

^{1}H NMR spectra were recorded with use of a Varian-VXR-300 spectrometer (300 MHz) at 25 °C in DMSO-d_6 solution. Chemical shifts are expressed in ppm (δ) relative to resonance of tetramethylsilane.

Elemental analysis was performed with use of an Elemental Analyzer EA 1110.

Ultraviolet absorption spectra of aqueous solutions of $Hg(NO_3)_2$ were recorded with a Specord M-40 spectrophotometer in the range from 260 to 400 nm. To record UV spectra quartz cells with $l = 1$ cm were used. Distilled water was the comparative solution.

---

* Corresponding author. Tel.: +380 444229691; fax: +380 444243567.
E-mail addresses: isc412@ukr.net, v-bel@mail.kar.net (O.M. Shvets).

0020-1693/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2008.10.004

X-ray diffraction analysis was performed on a DRON-4-07 diffractometer (Cu Kα radiation with a nickel filter).

The concentration of surface silanol groups of the silica adsorbents was calculated from the quantity of chemisorbed dimethylchlorosilane [14]. The amount of aminopropyl groups on the surface of organosilicas was determined by potentiometric titration (Ion-meter 1.120.1) and thermogravimetric analysis (Q-1500 D thermoanalyzer) [15,16]. The content of β-cyclodextrin immobilized on the surface of aminopropylsilica was assessed by differential thermogravimetric analysis with programmable heat [17].

The adsorption of Hg(II) ions from aqueous solutions was studied by using multibatch method under static conditions at 22 °C. Mercury(II) adsorption dependence on the time of contact with silicas and concentration of equilibrium solution was obtained. For adsorption experiments the mercury(II) nitrate solutions with concentration from 2.5×10^{-4} to 4.0×10^{-3} M (pH $\sim$ 1) were used. The batches of the silica adsorbents and the volumes of solutions of mercury(II) nitrate were 0.1 g and 20 cm^3, respectively.

The amount of Hg(II) ions in the initial and the equilibrium solutions was analyzed by atomic absorption spectrometry using a Pye Unicam SP-9 equipment and also with EDTA back-titration [18].

3. Results and discussion

Chemical immobilization of mono-tosyl-β-cyclodextrin (Ts-β-CD) onto the silica surface has been realized in two stages. The first step is modification of hydroxylated silica surface with aminopropyl groups. The second step is chemical reaction between aminopropylsilica and mono-tosyl-β-cyclodextrin.

3.1. Chemical modification of β-cyclodextrin with 4-toluenesulfonyl chloride

The synthesis of mono-tosyl-β-cyclodextrin was carried out by a reacting β-CD (1 mmol) dried at 105 °C during 14 h, with a solution of 4-toluenesulfonyl chloride (9.58 mmol) in dry pyridine at 4 °C for a period of 8 h, and then 24 h at room temperature [19,20]. Further, the reaction mixture was vacuum-dried at 40 °C up to formation of a crystalline precipitate. The precipitate was washed with diethyl ether, then recrystallized from hot water and dried in the air.

In the IR spectrum of β-cyclodextrin (Fig. 1) after contact with solution of 4-toluenesulfonyl chloride the absorption bands belonging to tosyl group, namely, the bands of the valence vibrations of the C=C bond in the benzene ring (600 cm^{-1}), the band of the asymmetric valence vibrations of the S=O bond in the R_1–O–SO_2–R_2 groups (1365 cm^{-1}), and also the band of the out-of-plane deformation vibrations of the C–H bonds in aromatic ring (815 cm^{-1}) are presented [21,22]. In the ^{1}H NMR spectrum of modified β-cyclodextrin the protons' signals of toluenesulfonyl group with chemical shifts δ (ppm) are registered: 2.433 (s) assigned to methyl radical of toluenesulfonyl group, and also the signals at 7.452 (d) and 7.747 (d) attributed to protons of benzene ring at 3,5 and 2,6 positions, respectively [23]. Hence, the reaction of electrophilic substitution of proton in alcoholic groups of β-cyclodextrin (first of all of the primary groups at position 6 [2,24,25]) by tosyl groups takes place between β-cyclodextrin and 4-toluenesulfonyl chloride.

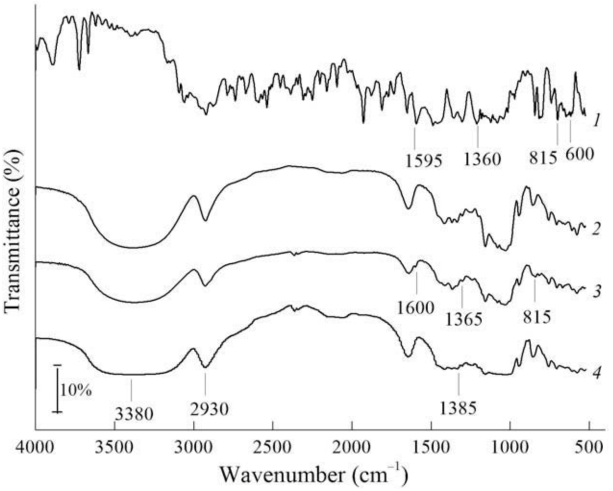

Fig. 1. IR spectra of 4-toluenesulfonyl chloride (1), β-cyclodextrin before (2) and after (3) interaction with 4-toluenesulfonyl chloride, inclusion complex of β-cyclodextrin with mercury(II) nitrate (*4*).

According to the data of elemental analysis only one alcoholic group of β-cyclodextrin molecule takes part in the reaction with 4-toluenesulfonyl chloride. Chemical modification of β-cyclodextrin with 4-toluenesulfonyl chloride is given in Scheme 1.

3.2. Chemical immobilization of mono-tosyl-β-cyclodextrin onto aminopropylsilica surface

For grafting of mono-tosyl-β-cyclodextrin the amino groups were preliminarily bonded onto the silica surface by the reaction with λ-aminopropyltriethoxysilane [26]. For this purpose Silochrome C-120 dried up at 200 °C for 6 h was placed into a three-necked reactor supplied with a stirrer and a reflux condenser, and suspended in a small amount of toluene during 40 min at room temperature. Then λ-aminopropyltriethoxysilane (three times in excess in relation to the content of silanol groups on a silica surface taken for modification) was added. The reaction mixture was stirred at 110 °C for 6 h. It was then left overnight at room temperature. Afterwards, the solid phase was transferred on a porous glass filter, washed with toluene until absence of silane (absence of a violet colour on addition of ninhydrin), then acetone, distilled water (for hydrolysis of the ether groups) and again acetone. The resulting aminopropylsilicas were dried in the air at 150 °C during 6 h. The aminopropylsilica synthesis is shown in Scheme 2.

The interaction of aminopropylsilica with mono-tosyl-β-cyclodextrin has been realized under optimal conditions for reaction of electrophilic substitution of proton in aminopropyl groups by β-cyclodextrin groups [25,27,28]. A batch of air-dried aminopropylsilica (2 g) was seated into the three-necked reactor supplied with a stirrer and a reflux condenser, and suspended in dry pyridine (20 cm^3) at room temperature under continuous stirring. Then, pyridine containing Ts-β-CD (0.25 g) was added (pH of reaction mixture ≅7). The reactor was placed in a hot water bath. The modification of the aminopropylsilica surface by Ts-β-CD was carried out at 60 °C during 4 days. Then the solid phase was moved on the porous glass filter, washed out by pyridine (25 $cm^3 \times 3$), acetone (25 $cm^3 \times 3$) and dried in the air.

In the IR spectrum of aminopropylsilica after interaction with solution of Ts-β-CD in pyridine at 60 °C (Fig. 2c, spectrum 5) the absorption bands of the valence vibrations of the O–H bonds in the secondary alcohol groups (3375, 3290 cm^{-1}), the C–H bonds of β-cyclodextrin (2950, 2880 cm^{-1}), and also the deformation vibrations of the N–H bond (1590, 1540 cm^{-1}) and C–H bond (1460 and 1390 cm^{-1}) are registered [21,29]. The absorption bands of the deformation vibrations in the primary and the secondary amino groups are presented. It is evidence of partial participation of the primary aminopropyl groups in the chemical grafting of Ts-β-CD. In the IR spectrum of modified silica the absorption bands of the valence vibrations of the C=C bond of benzene ring and the asymmetric valence vibrations of the S=O bond in the R_1–O–SO_2–R_2 groups are absence. Hence, the reaction of electrophilic