

Sol-gel Synthesis of β -Cyclodextrin-containing Silicas with 3-(chloropropyl)triethoxysilane as Precursor

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The sol-gel synthesis of β -cyclodextrin-containing silica materials is reported. Organosilicas were prepared in tetraethylorthosilicate–3-(chloropropyl)triethoxysilane– β -cyclodextrin–ethanol–water system. These materials were characterized by IR spectroscopy and thermogravimetric analysis. Porosity of organosilicas was characterized on nitrogen adsorption/desorption isotherms. The porosity analysis demonstrates that cyclodextrin-silica based materials are an isotherm Type I substance. The surface areas of the organosilicas with incorporated β -cyclodextrin are in the range 430–580 m² g⁻¹; materials containing up to 0.005 mmol g⁻¹ of β -cyclodextrin moieties have been successfully prepared. Synthesized organosilicas are stable in aqueous medium and could be used in processes of pollutants removal. The present study demonstrates a simple time-saving method of cyclodextrin-containing silicas obtaining via one-pot synthesis in mild condition without using toxic solvents, costly templates or cyclodextrin derivatives.

Keywords: Sol-gel synthesis, Silica, Incorporation, β -Cyclodextrine, Tetraethylorthosilicate, 3-(chloropropyl)triethoxysilane.

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1. INTRODUCTION

Amongst the numerous organic materials, metal surfaces or inorganic oxide supports, silica has a high potential for creation functional nanomaterials owing to its physical and chemical properties. The aim of study cyclodextrin(CD)/silica materials preparation is twofold. The first is the possibility of CDs utilization as template (porogen) in the synthesis of porous substances with regular structure (so-called, nanocasting) [1-4]. Here, “worm-type” pore system is formed [1-2, 5]. Amphiphilic nature of CDs and their high water solubility [4] are defining properties for using CDs as porogens. The second is the application of CD/silica compositions as carriers in liquid chromatography or adsorbents for water purification [6]. Here, CDs water solubility is unacceptable. Therefore, formation of strong binding between CD moiety and silica surface is one of the main requirements in the application fields of CD-containing materials. There are three pathways for CDs embedding in silica structure. The first two (coating and grafting methods) are based on the use of ready-made support [7-14]. They are studied and described in detail. The third approach supposes the introduction of CD moiety into the siliceous framework directly during the synthesis of silica material. A few investigations devoted to this approach have been described in the literature. This procedure, as a rule, is realized by sol-gel synthesis with costly templates and CDs derivatives using [5, 8, 15]. Such materials were tested in processes of pollutants removal from aqueous media [5, 8-10, 16-18].

In this research, we report attempts at preparing CD-containing silicas from pristine β -cyclodextrin and a mixture of alkoxy silane compounds by sol-gel method. These materials were characterized by IR spectroscopy and N₂ sorption experiments. The probably effective-

ness of CD-containing silicas from these approaches for adsorption of aromatic molecules is discussed.

2. EXPERIMENTAL

2.1 Synthesis

Sol-gel materials were prepared by the acidic hydrolysis (0.1M HCl) of tetraethylorthosilicate (TEOS) or TEOS/3-(chloropropyl)triethoxysilane(CPTEOS) blend in ethanol. The molar ratio 5 : 1 and 8 : 1 of alkoxy silanes were used. CD-functionalized materials were obtain by agitation a β -CD and alkoxy silanes compounds together with a solvent (C₂H₅OH) to give a mixture. The reaction mixture was blended on magnetic stirrer about 20 min. Then the appropriate amount of water was added to cause hydrolysis of the alkoxy silane compounds and gelation of the hydrolyzate to give a uniform gelled mass. Gelling of sols was carried out via ageing at 70 °C up the viscosity of the solution was gradually increased and was finally gelled and solidified into a jelly-like uniform mass. Also the gelling of sols was realized via hydrothermal treatment (HTT) in autoclave at 150 °C during 3 h. Obtained xerogels were washed by water and dried at ambient temperature.

2.2 Analysis

Infrared spectra were registered in the range from 4000 to 400 cm⁻¹ using Thermo Nicolet NEXUS FTIR spectrophotometer equipped with an environmental chamber for selector DRIFT. The spectra were performed in KBr pellets with 1 : 20 ratio of sample and KBr, respectively.

Porosity measurements were obtained with a Nova 1200 apparatus from Quantachrome Corporation. Specific surface areas were determined using the BET

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method. The pore volumes and the pore size distributions were obtained using BJI isotherm.

Thermogravimetric analysis was carried out on a Derivatograph-Q (MOM, Budapest) in the temperature range 30–600 °C with a heating rate of 10° min⁻¹.

The content of β -CD in organosilicas was determined with acid hydrolysis of cyclodextrin up to glucose. The concentration of glucose after the reaction with potassium ferrocyanide was defined by spectrophotometry using Specord M-40 equipment (Germany, Carl Zeiss Jena) at $\lambda = 420$ nm [19].

3. RESULTS AND DISCUSSIONS

The possibility of preparing CD-silica by using sol-gel approach has been recently proposed. CD-silica composite was prepared by the hydrolysis and silanol condensation of TEOS in the presence of CD to give a gelled siliceous mass, into which molecules of CD are incorporated presumably or mostly by forming Si–O–C linkages [20].

Our aim was to obtain stable in aqueous media CD-containing silicas with using functional silanes and unmodified β -CD. It was shown that CD-containing silicas prepared from TEOS in water-ethanol solution with acid catalyst are hydrolytically unstable and could not be used as adsorbents for the removal of toxic contaminants from water.

In the DRIFT spectra of washed silica obtained from β -CD/TEOS mixture in the range 3800–3150 cm⁻¹ there is no clear maximum as in the spectra of β -CD and

β -CD-containing xerogel, which is likely to cause the valence vibrations of the O–H bonds in the hydroxyl groups of β -CD connected by hydrogen bonds. Also, the band with absorption maximum at 2932 cm⁻¹ (valence vibrations of the C–H bonds in the CH and CH₂ groups of β -CD molecules) disappears in washed xerogel. The band assignments in the DRIFT spectra of β -CD

and β -CD-containing xerogel in the interval 1400–500 cm⁻¹ showed, that only in unwashed xerogel absorption bands of β -CD groups are present. Thus, in the region 1400–1200 cm⁻¹ the absorption bands of the deformation vibrations δ_{C-H} in the primary and secondary hydroxyl groups of β -CD are registered. In the interval 1200–1030 cm⁻¹ the absorption bands of the valence vibrations of the C–O bonds in the ether and hydroxyl groups of β -CD (1078 and 1030 cm⁻¹) are observed. The absorption bands in the range 950–700 cm⁻¹ belong to deformation vibration δ_{C-H} and the pulsation vibrations in the glucopyranose cycle.

The drastic decrease of β -CD moieties on the surface of prepared materials was also confirmed by chemical analysis. Hence, it is obvious that hydrolytically unstable Si–O–C linkages are formed as a result of sol-gel synthesis of CD-containing silicas from TEOS and CD.

3.1 FTIR spectrophotometry

Hydrolytically stable CD-containing silicas could be prepared by hydrolysis and polycondensation of TEOS and CPTEOS. In the presence of CPTEOS stronger C–O–C linkages are possible to form.

Infrared spectra of pristine silica, functionalized organosilica and CD-containing silica are shown in Figure 1. The silanol groups disposed on the silica surface and the presence of remaining water molecules produce the broad stretching band around 3046 cm⁻¹, followed by a band around 1640 cm⁻¹, attributed to deformation vibration δ_{O-H} . A strong absorption band near 1100 cm⁻¹, attributed to asymmetric stretching of Si–O–Si bonds, is observed in all silica samples. When analyzing organosilica materials, the presence of absorption band of deformation vibrations of the C–H bonds at 1443 cm⁻¹ is observed. After the hydrolysis and polycondensation of TEOS/CPTEOS mixture both in the absence and presence of β -CD, the characteristic bands in the region 1400–1200 cm⁻¹ and 1200–900 cm⁻¹ are appeared in the spectra of silica materials. These bands related to the valence vibrations of the C–O, C–OH, and C–O–C bonds as well as deformation vibrations of the C–H bonds. Indication of the presence of CDs on silica is the appearance of specific vibration band ascribed to β -CD at 2943 cm⁻¹.

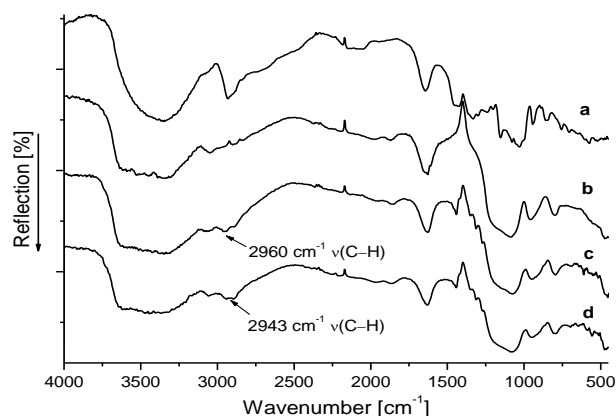


Fig. 1 – DRIFT spectra of β -cyclodextrin (a) and silicas prepared from TEOS (b), TEOS/CPTEOS=5 : 1 (c), and cyclodextrin-silica based material (d)

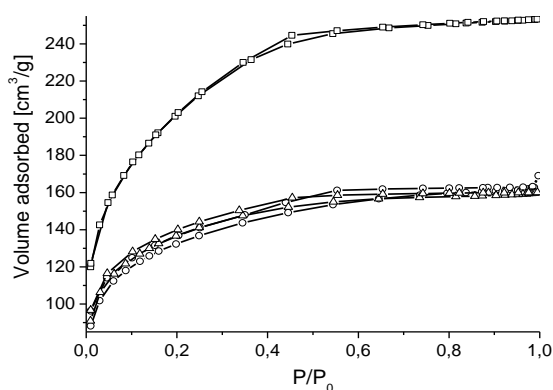
The band assignments in DRIFT spectra confirm the presence of β -CD on the surface of synthesized materials. Since the primary hydroxyl groups of the β -CD are more nucleophilic, more basic and less sterically hindered than the secondary hydroxyls, the primary hydroxyl groups exhibit also greater reactivity. Consequently, CDs are predominantly attached via this group and an appropriate spacer to the surface [21]. However, the formation of C–O–C bound with participation of the secondary hydroxyl groups of β -CD is not excluded.

3.2 Structural characterization of sol-gel CD-silica composites

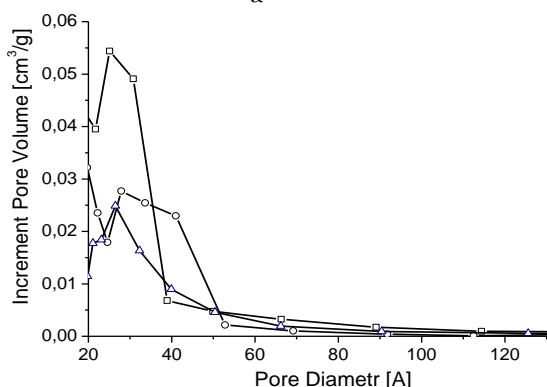
Texture is one of the main characteristics, which could explain later the behaviour of materials in decontamination applications. Figure 2 shows the nitrogen adsorption and desorption isotherms of the pristine silica and functionalized silicas. The textural characteristics derived from N₂ adsorption/desorption experiments of studied materials are summarized in Table 1.

Table 1 – Physical and surface properties of cyclodextrin silica-based materials

| Sample | TEOS/ CPTEOS ratio | Synthesis condition | Surface area ($\text{m}^2 \text{g}^{-1}$) | Total specific mi- cropore volume V_{micro} ($\text{cm}^3 \text{g}^{-1}$) | Total specific mesopore volume V_{meso} ($\text{cm}^3 \text{g}^{-1}$) | CD con- tent ($\mu\text{mol g}^{-1}$) |
|----------------------|--------------------------|------------------------|---|--|--|---|
| Silica | – | 70 °C | 863 | 0,033 | 0,291 | – |
| Silica | – | 150 °C, 3h | 720 | 0,044 | 0,206 | – |
| Silica – CPTEOS | 8 : 1 | 70 °C | 530 | 0,129 | 0,198 | – |
| Silica – CPTEOS | 8 : 1 | 150 °C, 3h | 489 | 0,124 | 0,188 | – |
| Silica – CPTEOS | 5 : 1 | 70 °C | 396 | 0,084 | 0,171 | – |
| Silica – CPTEOS | 5 : 1 | 150 °C, 3h | 470 | 0,081 | 0,155 | – |
| Silica – β -CD | 8 : 1 | 70 °C | 533 | 0,129 | 0,202 | 3,54 |
| Silica – β -CD | 8 : 1 | 150 °C, 3h | 577 | 0,131 | 0,131 | 2,76 |
| Silica – β -CD | 5 : 1 | 70 °C | 429 | 0,107 | 0,177 | 4,83 |
| Silica – β -CD | 5 : 1 | 150 °C, 3h | 485 | 0,083 | 0,134 | 2,66 |



a



b

Fig. 2 – N_2 adsorption-desorption isotherms (a) and pore size distribution (b) for pristine SiO_2 (square symbol), silica prepared from TEOS/CPTEOS as precursors (circle symbol), and CD-silica composite (triangle symbol)

According to the common classification of adsorption isotherms, the isotherms for all synthesized silicas are considered Type I. It could be concluded that there are no drastic changes in the morphology of materials. However, isotherms of silica prepared from TEOS/CPTEOS mixture and CD-silica composite exhibited narrow hysteresis loops in the wide range of P/P_0 . This hysteresis is not seen in the isotherm of pristine silica prepared from TEOS. The appearance of hysteresis loops could be explained by the presence of both micro and mesopores. The pore size distribution (Figure 2(b)) estimated from the desorption branch of the isotherm is narrower for pristine silica and CD-silica composite

with the average pore diameter 2,5 nm. As expected, the specific surface area decreases for materials with higher TEOS/CPTEOS molar ratio. The total volume of micropores obtained from BJH model increases in the case of silica functionalization.

It was stated above that the characteristic FTIR bands qualitatively denoting the successful incorporation of CD groups into the silica frameworks. The presence of β -CD on the surface of prepared materials was confirmed by chemical analysis. The content of β -CD in organosilicas is shown in the Table 1. Compared to CD-silica materials with TEOS/CPTEOS = 8 : 1 molar ratio of initial solution, the higher CD group loadings can be achieved using the molar ratio 5 : 1.

3.3 Thermal analysis of CD-containing materials

The three series samples (silicas from TEOS, silicas from TEOS/CPTEOS mixture, and CD-silicas from TEOS/CPTEOS mixture) in our study have different thermal stability. Generally, it could be distinguished two main regions in thermogravimetric curves of all silicas. The region up to 150 °C corresponds to desorption of physically adsorbed water or perhaps residual solvent. The principal weight loss is observed in the region after 150 °C, and is related to the removal of organics accompanied by polymerization, structural relaxation, and bond shrinkage.

For the silicas, prepared from the hydrolytic condensation of TEOS, desorption of physically adsorbed water is observed at 100 °C. Then the slow structure reorganization is occurred. Organosilicas have more drastic weight loss in the region 235–480 °C. According to the thermogravimetric results obtained on CD-silica materials, the temperature, for which the rate of weight loss was the most significant, was about 295 °C. This weight loss correlates with the thermal degradation of CD moieties on silica surfaces [12].

4. CONCLUSION

Hydrolytically unstable Si–O–C linkages are formed as a result of sol-gel synthesis of CD-containing silicas from TEOS and CD. Hydrolytically stable CD-containing silicas were prepared by hydrolysis and polycondensation of TEOS and CPTEOS, where the stronger C–O–C linkages are formed. The band as-

signments of DRIFT spectra confirm the presence of β -CD moieties in organosilicas. The porosity analysis demonstrates that CD-silica based materials are an isotherm Type I substance and pore size distribution with a small maximum at 2.5 nm. The surface areas of the organosilicas with incorporated β -CD are in the range 430–580 m² g⁻¹; materials containing up to 0.005 mmol g⁻¹ of β -CD moieties have been successfully prepared. Thermogravimetric analysis of CD-containing materials reveals an important weight loss in the temperature range 235–480 °C, corresponding to

the progressive decomposition of the organic moieties.

Although synthesized organosilicas show smallest CD group loadings in comparison with known CD-containing materials, they were obtained via a simple sol-gel technique in one-pot synthesis, which does not require high temperatures, toxic organic solvents and a huge investment of time.

Direct sol-gel synthesis of hydrolytically stable CD-containing silicas can therefore be considered for the preparation of sorbents for effective separation and removal of aromatic compounds from aqueous media.

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