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A water soluble 3-n-propyl-1-azonia-4-azabicyclo[2.2.2]octanechloride silsesquioxane grafted onto Al/SiO2 surface. Chromium adsorption study

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Abstract: The water soluble material, 3-n-propyl-1-azonia-4-azabicyclo[2.2.2]octanechloride silsesquioxane (dabcosil silsesquioxane) was obtained. The dabcosil silsesquioxane was grafted onto a silica surface, previously modified with aluminum oxide. The resulting solid, dabcosil-Al/SiO_2, presents 0.15 mmol of dabco groups per gram of material. The product of the grafting reaction was analyzed by infrared spectroscopy and N_2 adsorption-desorption isotherms. The dabcosil-Al/SiO_2 material was used as sorbent for chromium (VI) adsorption in aqueous solution.

Keywords: dabco; sol-gel; chromium (VI).

Introduction

In the last two decades a considerable attention has been devoted to the preparation of immobilized organic groups on silica gel surfaces that can be used as sorbent materials. The primary grafting reaction has been well studied [1-4]. This technique involves the immobilization of the organic group using an organosilane as a coupling reagent [5-7]. The resulting solids present a strong covalent bonded organic phase [7]. However, in the last decade hybrid materials obtained by using the sol-gel method became as an alternative to obtain organofunctionalized silicas [8-10]. The sol-gel synthesis for this kind of materials is based on the hydrolysis and polycondensation of organosilanes in the presence of tetraethylorthosilicate or tetramethylorthosilicate [11]. The hybrids obtained present also a strongly bonded organic phase [12,13] and they show some advantages when compared with the grafted materials, since the synthesis can be performed at room temperature and the resulting solids have good homogeneity and purity. Additionally some properties like organic content, surface area, pore size and particle size can be controlled starting from the choice of the synthesis conditions [13,14]. Among the sol-gel silica based materials the silsesquioxanes are an interesting class of materials that contain a high degree of pendant or bridged organic groups [15,16].

In previous papers, the preparation of a silsesquioxane water soluble material was reported [17]. It was obtained by using n-propylpyridinium chloride as pendant group. Besides its high water solubility, a very important characteristic of this material was its capacity for forming a stable thin film on surfaces containing aluminum oxide [18]. Recently, we have obtained another water soluble material, the 3-n-propyl-1-azonia-4-azabicyclo[2.2.2]octanechloride silsesquioxane (dabcosil silsesquioxane) [19,20]. It was observed that this material is constituted by oligomeric species and its solubility is a consequence of the ion dipole interactions between the azonia salt with water molecules [20].

In the present work we have combined the sol-gel method and the grafting technique in the preparation of new hybrid materials. The dabcosil silsesquioxane was synthesized by using the sol-gel process and subsequently it was grafted onto a silica gel surface, previously modified with aluminum oxide. The resulting material was characterized by using infrared spectroscopy, N_2 adsorption-desorption isotherms and its sorption capacity was evaluated for chromium (VI) uptake in aqueous solution.

Experimental

Synthesis of 3-n-propyl-1-azonia-4-azabicyclo[2.2.2]octanechloride silsesquioxane (dabcosil)

An amount of 2.244 g (10 mmol) of 1,4-diazabicyclo[2.2.2]octane (dabco, Acros), previously sublimed, were dissolved in 40 ml of an ethanol:acetone (Merck) solution (1:1), and 20 mmol (3.8 ml) of 3-cloropropyltrimethoxysilane (CPTMS, Acros) were added. This mixture was refluxed, in argon atmosphere under stirring, at near 90 ºC for 48 h. The product of reaction, 3-n-propyltrimethoxysilane-1-azonia-4-azabicyclo[2.2.2] octanechloride was used as organic precursor in the sol-gel synthesis. In the previous solution it was added, under stirring, tetraethylorthosilicate (TEOS, Acros) (3.7 ml), twice distilled water (3.9 ml) and HF (0.1 ml). The mixture was stored for 15 days, just covered without sealing. The gel was then washed with acetone and dried at 90 ºC for 1.5 h.

Synthesis of aluminum oxide grafted onto silica gel surface (Al/SiO$_2$)

Aluminum isopropoxide (Aldrich) (1.24 g) were dissolved in 50 ml of hot toluene (Merck). An amount of 10 g of silica gel (Merck) was previously activated in vacuum at 150 ºC. The silica was added to aluminum isopropoxide solution. The mixture was stirred for 24 h, in argon atmosphere, under reflux conditions. The resulting product was filtered, washed with toluene, ethanol, ethyl ether and evaporated in vacuum at 110 ºC. To promote the hydrolysis, the product was immersed in twice distilled water and promptly filtrates, washed with water and finally dried in vacuum at 120 ºC.

Synthesis of dabcosil silsesquioxane grafted onto Al/SiO$_2$ surface (dabcosil-Al/SiO$_2$)

The dabcosil silsesquioxane (300 mg) was dissolved in twice distilled water (100 ml) and soon it was added to 5 g of Al/SiO$_2$. The mixtures were shaken for 15 min and the water was then evaporated, in vacuum, at temperature of 120 ºC.

Elemental analysis

The organic phase content on dabcosil silsesquioxane was obtained using a CHN Perkin Elmer M CHNS/O Analyzer, model 2400. The analysis was made in triplicate, after heating the material at 100 ºC, under vacuum, for 1 hour. The amount of dabcosil groups presents on the dabcosil-AlSiO$_2$ surface was estimated as follows: the material was immersed in HNO_3 solution, under stirring, the acid solution was then submitted to chloride potentiometric titration with silver nitrate, using calomel electrode, as reference. The aluminum content in the Al/SiO$_2$ was estimated employing EDS (electron dispersive spectroscopy) analysis using a Noran detector in JEOL equipment, model JSM 5800, with 20 kV and acquisition time of 100 s and 800x of magnification.

FTIR analysis

Samples of silica gel, aluminum oxide grafted onto silica gel (Al/SiO$_2$) and dabcosil silsesquioxane grafted onto Al/SiO$_2$ materials were submitted to transmission FTIR using an IR cell described elsewhere in detail [7]. Self-supporting disks of materials with an area of 5 cm^2, weighing *ca*. 100 mg, were prepared. The disks were heated for 1 hour at 150 ºC, under vacuum of 1 Pa (near 10^{-2} torr). The spectra were obtained using a Shimadzu equipment model FTIR 8300, with 4 cm^{-1} of resolution and 100 scans.

Pore size distribution

The pore size distribution was obtained by the N_2 adsorption-desorption isotherm, determined at liquid nitrogen boiling point, using a homemade volumetric apparatus, connected to turbo molecular Edwards vacuum line system, employing a Hg capillary barometer. The apparatus is frequently checked with alumina standard reference. The hybrid material was previously degassed at 150 °C, in vacuum, for 2 h. The data analysis was made using the BJH (Barret, Joyner, and Halenda) method [21].

Surface area

The specific surface area of the previous degassed solid at 150 °C, under vacuum, was determined by the BET (Brunauer, Emmett and Teller) multipoint technique [22], in the volumetric apparatus cited above, using nitrogen as probe, in triplicate.

Chromium (VI) uptake by the dabcosil-Al/SiO$_2$

An aliquot of 20.00 ml of 20.00 – 1000.0 mg l^{-1} Cr (VI) (in CrO_4^{2-} form at pH 6.0) was added to a conical plastic tube (117mm height, 30 mm diameter) containing 50.0 mg of dabcosil-Al/SiO$_2$. The flasks were capped, in poured horizontally in a horizontal shaker and agitated for 3 h. Afterwards the flasks were filtered, using glass filter provided with Whatman filter paper, in order to separate the adsorbent from the aqueous solution, and aliquots of 1-5 ml the supernatant were properly diluted to 50-100 ml in calibrated flasks using water. The chromium final concentrations were spectrophotometrically determined using diphenylcarbazide at 540 nm [23], after multiplying the measured concentration value found in the solution after the adsorption procedure, by the proper dilution factor.

The amount of Cr (VI) uptaken by the adsorbent is given by the equation 1.

$$Nf = \frac{(Co - Cf).V}{m} \tag{1}$$

Where Nf is the amount of metallic ion uptaken by the adsorbent (mmol g^{-1}); Co is the initial Cr (VI) concentration put in contact with the adsorbent (mmol l^{-1}), Cf is the Cr (VI) concentrations (mmol l^{-1}) after the batch adsorption procedure, m is the mass of adsorbent (g) and V is the volume of Cr (VI) solution put in contact with the adsorbent (l).

Results and discussion

The synthesis of the dabcosil silsesquioxane was carried out in two steps. Firstly the 3-n-propyltrimethoxysilane-1-azonia-4-azabicyclo[2.2.2]octanechloride was obtained from a presumable SN$_2$ reaction of dabco with CPTMS. In a second step, this compound was added to a TEOS solution to gelation, as already reported [19]. The product of the gelation reaction, 3-n-propyltrimethoxysilane-1-azonia-4-azabicyclo[2.2.2]octanechloride silsesquioxane (dabcosil silsesquioxane) was submitted to CHN elemental analysis and the estimated organic phase content was 3.3 mmol of dabcosil groups per gram. Considering the high water solubility of the dabcosil silsesquioxane [20] it could be immobilized on the Al/SiO$_2$ matrix having an Al/Si atomic ratio of 0.21, determined by EDS analysis. The dabcosil groups present on dabcosil-Al/SiO$_2$, estimated by using chloride potentiometric titration, was 0.28 mmol of dabcosil pendant groups per gram of AlSiO$_2$ matrix.

The infrared spectra of the pure silica (SiO$_2$), aluminum oxide grafted onto silica surface (Al/SiO$_2$) and dabcosil grafted onto Al/SiO$_2$ surface (dabcosil-Al/SiO$_2$) are shown in the Figure 1. It is possible to observe in the pure

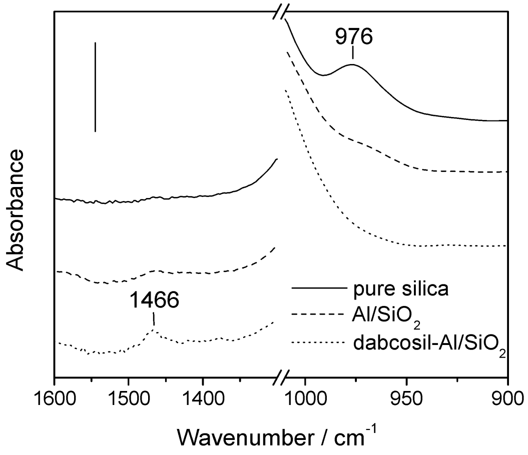

Figure 1. Infrared absorbance spectra obtained at room temperature after being heated at 150 °C, in vacuum, for two hours. a) SiO$_2$; b) Al/SiO$_2$; c) dabcosil-Al/SiO$_2$. The bar value is 0.5.

silica spectrum (Spectrum a) that the band at 976 cm^{-1}, assigned to Si-OH stretching mode [24], disappears after the grafting reaction with the aluminum oxide (spectrum b). This result is an indication that the silanol groups of the original silica surface were covered by the aluminum oxide [25]. In the spectrum obtained for dabcosil-Al/SiO_2 (spectrum c) it is possible to observe the organics presence identified by the bending CH_2 modes of the dabco group in 1466 cm^{-1} [26].

The grafting reactions could also be evidenced on the pore size distribution obtained from the N_2 adsorption-desorption isotherms, showed in Figure 2. It is possible to observe that pure silica (SiO_2), aluminum oxide grafted onto silica surface (Al/SiO_2) and dabcosil grafted onto Al/SiO_2 surface (dabcosil-Al/SiO_2) present similar pore size distribution with a maximum near to 8 nm. The BET surface area values were also very similar: 200, 200 and 190 m^2 g^{-1} for SiO_2, Al/SiO_2 and dabcosil-Al/SiO_2, respectively. Considering a deviation of 5 % in these measurements, the surface areas are constant and indicate that the grafting reactions occur homogeneously in the surface, possibly forming monolayer.

The dabcosil-Al/SiO_2 material obtained was used as adsorbent for chromium (VI) uptake from aqueous solution. The monolayer Langmuir model was applied to the system using the Langmuir linearized model (equation 2), where Nf is the amount adsorbed of Cr (VI) (mmol g^{-1}) at the equilibrium, Ce is the concentration of Cr (VI) not adsorbed left in the solution after the equilibration (mmol l^{-1}), Qmax is the maximum adsorptive capacity of the Cr (VI) (mmol g^{-1}), b is the Langmuir constant related to the energy of adsorption (l mmol^{-1})

$$\frac{Ce}{Nf} = \frac{1}{b.Q\max} + \frac{1}{Q\max}Ce \qquad (2)$$

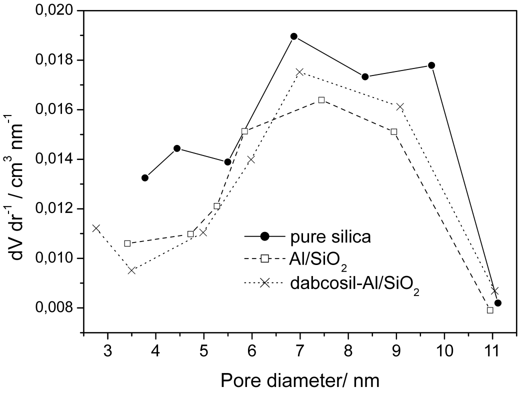

Figure 2. Pore size distribution, obtained from N_2 desorption isotherms, by using BJH method.

By applying this linear model (Ce/Nf versus Ce) the Qmax obtained was 0.144 mmol g^{-1} and b was 0.305 l mmol^{-1}, with r= 0.9932 (see fig 3).

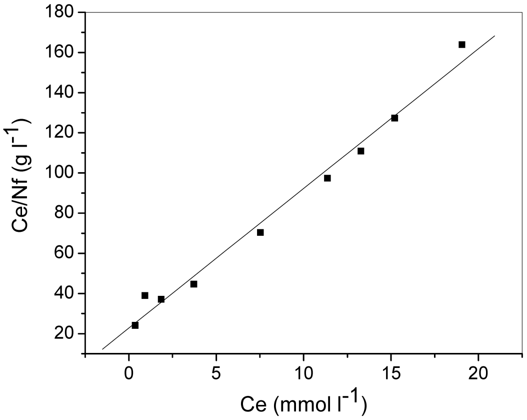

Figure 3. Linearized Langmuir model for Cr (VI) uptake by dabcosil-Al/SiO_2.

Taking into account the amount of dabcosil groups present on the material which was 0.28 mmol g^{-1} and the maximum amount of Cr (VI) as chromate uptaken by the adsorbent (0.144 mmol g^{-1}), it could be inferred that the mechanism for Cr (VI) uptake by the adsorbent was a ion exchange of two Cl$^-$ anion by one CrO_4^{2-}. Each CrO_4^{2-} replaced two Cl$^-$ present in the adsorbent. It should be mentioned that at pH 6.0, Cr(VI) is mainly present in CrO_4^{2-} form and it is present in small amounts as $HCrO_4^-$ and $Cr_2O_7^{2-}$. However the isotherm fits very well the Langmuir model, it is expected that only CrO_4^{2-} is the chemical specie that is being adsorbed by the dabco groups.

Considering the maximum amount of Cr(VI) uptaken and the amount of dabco groups obtained in elemental analysis, all dabcosil groups were available on the surface of the material that were able for ion exchange. On the other hand, in previous reports of synthesis of dabco by the sol-gel method [14], the dabco groups were not completely available for adsorption that resulted in a decrease in the maximum amount of metallic ion uptake by the adsorbent.

Conclusion

The water soluble 3-n-propyl-1-azonia-4-azabicyclo[2.2.2]octanechloride silsesquioxane was immobilized on silica previously modified with aluminum oxide in a highly dispersed form. The dabcosil-Al/SiO_2 material showed to be a good adsorbent for Cr (VI) uptake from aqueous solution, where for each two mmol dabcosil group grafted at the Al/SiO_2 matrix was able to adsorb one mmol of Cr (VI) as chromate from aqueous solution, suggesting an ion exchange mechanism.

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L. T. Arenas, N. M. Simon, Y. Gushikem, T. M. H. Costa, E. C. Lima, E. V. Benvenutti. Silsesquioxano solúvel em água, cloreto de 3-n-propil-1-azônia-4-azabiciclo[2.2.2]octano, enxertado sobre a superfície de Al/SiO_2. Estudo da adsorção de cromo.

Resumo: O material octanocloreto de 3-n-propil-1-azonia-4-azabiciclo[2.2.2] silsesquioxano (dabcosil silsesquioxano) solúvel em água foi obtido. O dabcosil silsesquioxano foi enxertado na superfície da sílica, previamente modificada com óxido de alumínio. O material sólido resultante dabcosil-Al/SiO_2, apresentou 0,15 mmol de grupamentos dabco por grama do material. O produto enxertado foi caracterizado por espectroscopia de infravermelho, e isotermas de adsorção-dessorção de N_2. O material dabcosil-Al/SiO_2 foi utilizado como sorvente para a adsorção de chromium(VI) em soluções aquosas.

Palavras-chave: dabco; sol-gel; cromo (VI).

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