



Inorganic–organic hybrids presenting high basic center content: SBA-15 incorporation, toxic metals sorption and energetic behavior

Fernando J.V.E. Oliveira^a, Maurício A. Melo Jr.^b, Claudio Airoidi^{b,*}

^a Departamento de Química, Universidade Federal da Paraíba, 58059-900 João Pessoa, PB, Brazil

^b Institute of Chemistry, University of Campinas, UNICAMP, P.O. Box 6154, 13084-971 Campinas, São Paulo, Brazil

ARTICLE INFO

Article history:

Received 2 August 2012

Received in revised form 23 October 2012

Accepted 25 November 2012

Available online 3 December 2012

Keywords:

A. Inorganic compounds

A. Structural materials

A. Surfaces

B. Sol–gel chemistry

D. Surface properties

ABSTRACT

Mesoporous SBA-15 samples were organofunctionalized with mono, di- and tri-aminosilanes that previously reacted with thiocarbamide to enhance the organic chains and attach nitrogen and sulfur basic centers to the surface of the solids. These new organosilanes were synthesized through a non-solvent approach to reduce both cost and hazardous wastes. The high affinities for both hard and soft Lewis acids due to the combination of nitrogen and sulfur atoms attached to the same pendant chain enabled favorable sorption capacities for Cu^{2+} , Cd^{2+} and Pb^{2+} cations, with maximum capacities of 1.90, 3.48 and 5.30 mmol g^{-1} , respectively, for the most efficient mesoporous silica. Microcalorimetric investigations allowed the calculation of the thermodynamic data at the solid/liquid interface. All Gibbs energy are negative as expected for spontaneous cation/basic center interactions and the positive entropic values from 49 ± 3 to $108 \pm 5 \text{ J K}^{-1} \text{ mol}^{-1}$, also reinforced this favorable interactive process in heterogeneous system. The designed organosilanes covalently bonded to the inorganic siliceous skeleton can be suggested as new materials for toxic metal removal from a wastewater with high efficiency.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Over the last two decades mesoporous materials have reached great status not only in academia, but also in industrial applications [1,2]. Mesoporous silica-based solids have attracted much attention due to their unique properties, which are provided by soft conditions from the sol–gel process [3–5]. This process, combined with template techniques, permits a great variety of mesostructured materials, according to the fine-tuning of the experimental parameters [6]. Thus, different pore wall structures and morphologies can be achieved by using this approach, which benefits from the sol–gel versatility so that different morphologies, such as powders, films, monoliths and nanoparticles have been synthesized [7].

These synthesized compounds are known as hybrids, due to their adequate inorganic–organic association, a feature that combines both inorganic and organic properties, and has resulted in an improvement of thermal, mechanical and chemical stability of the final compounds. These hybrid compounds are classified in two distinct categories. The first one, class I, is composed of materials that are held together by weak forces as van der Waals, hydrogen bonding, electrostatic (London) and π – π interactions. On the other hand, compounds that present covalent bonds

between the organic and inorganic parts belong to class II, with functional groups inserted onto the porous silica framework [8,9].

A critical challenge in this field is to design hybrid materials that present functional chemical groups on the porous surface walls. Taking into account the template approach, the most used methods are co-condensation and post-grafting synthetic procedures [10,11]. Based on the established general principles of the first method, the functional silane is added to a mixture of tetraethoxysilane (TEOS) and surfactant, with a concomitant formation of the final functionalized structure. Considering the post-grafting procedure, the ordered mesoporous skeleton is first obtained, and the desired silane is added to the suspension in a second step to result in the final functional solid. Although a large number of mesoporous silica have been reported, there is less information on the development of new modified organosilanes that contain specific groups attached to pendant chains inside the pore walls. In general, the reaction between the silane and a ligand improves the basicity of the network by increasing the number of Lewis basic sites, which reflects in their ability for heavy metals sorption capacity [12–14].

Taking into account the interest in the inorganic–organic hybrid research field, the reactions of thiocarbamide with three different silanes in a non-solvent system, to provide new possibilities to obtain such solids was investigated. The present procedure was first developed for silica gel functionalization [15], whose promising results inspired application to the well-known properties of mesoporous SBA-15.

* Corresponding author. Tel.: +55 19 35213055; fax: +55 19 35213023.
E-mail address: airoidi@iqm.unicamp.br (C. Airoidi).

Bearing in mind the applicability of such synthetic materials for toxic metal removal, which is an important challenge in wastewater treatment to eliminate these highly toxicity agents, a high level of sorption capacity even at extremely low concentration is required [16]. These metallic pollutants are found in industrial process rejects, mainly present in mining, paints and dyeing applications. Several procedures are known to be effective for metal removal, such as ion exchange, precipitation, reverse osmosis, and sorption [17–19]. Although all of these methods present good performance for this purpose, sorption process seems to be highlighted because of their low cost associated with experimental facility. A widespread sorbent is activated charcoal, which is obtained from diversity of abundant raw sources and at relatively low cost, and shows good performance [20]. However, in recent years, a lot of reports have described alternatives for replacing it, such as novel inorganic–organic hybrids, which usually present enhanced properties of sorption capacity for a series of toxic metal ions. Mesoporous silica hybrids are some of the most studied classes of materials for sorption processes, due to their desirable properties as high surface area and pore volume, high ordered pore arrangement and great mechanical and thermal stability [21,22].

Most of the research groups that are interested in preparing high performance sorbent solids employ silylating agents [23]. Normally, these chemicals can be purchased, and there are many options concerning the functional terminal group. However, publications report subsequent modifications of those terminal functions by inserting new ligands, which provide considerable improvements on the basicity of the resulting solid [24–26].

Metal ions play the role of Lewis acidities in sorption systems and are suitable to interact with Lewis bases attached to pendant chains. Thus, this investigation presents a non-solvent approach for modifying organosilanes with thiocarbamide, which afterwards is covalently bound to the SBA-15 backbone and used for copper, cadmium and lead removal from aqueous solutions. The cation/basic center interactions were followed calorimetrically in order to determine the thermodynamic data, to help the analyses of the energetics involved at the solid/liquid interface [27,28].

2. Materials and methods

2.1. Chemicals

The alkoxysilanes 3-aminopropyltriethoxysilane (N), N-[3-(trimethoxysilyl)-propyl]ethylenediamine (2N) and N-[3-(trimethoxysilyl)propyl]diethylenetriamine (3N), triblock copolymer Pluronic[®] P123 (EO₂₀PO₇₀EO₂₀) and all metallic nitrate salts were purchased from Sigma–Aldrich and were used as received. Thiocarbamide (t), ammonium sulfate, as well as other chemicals, were purchased from Synth and used without further purification. For the sorption experiments, deionized water was obtained from an ultra-pure Milli-Q 18.2 MΩ cm⁻¹ system. The copper, cadmium and lead solutions were prepared from the nitrate salts, in deionized water.

2.2. Syntheses

The mesoporous silica was synthesized according to a published procedure [29]. SBA-15 was prepared by mixing 4.0 g of pluronic P123 with 120 g of 2.0 mol dm⁻³ hydrochloric acid and 30 g of distilled water. This suspension was magnetically stirred for 4 h, at 310 K. After polymer dissolution, 8.25 g of TEOS was slowly dropped into the polyethylene beaker, and left under the same conditions as before for 1 h, then the mixture was transferred to a stainless steel autoclave, where it was kept at 373 K for 24 h. The white solid was filtered, washed with ethanol and water, and the template was removed by calcinations at 813 K for 5 h.

The silanes containing from one to three nitrogen atoms were reacted with thiocarbamide in a 2:1 molar ratio, in absence of solvent. This ratio is based on the possibility of reacting both amino groups from the thiocarbamate with the silane pendant chains. In this condition, the best suitable amount of each silane for acting as a solvent was determined as 20.0 cm³ (85.4 mmol), in case of the aminosilane N. To follow the proposed stoichiometry, 3.25 g (42.7 mmol) of thiocarbamide was used, and therefore, 30 mg of (NH₄)₂SO₄ was added to the flask. The system was kept under magnetic stirring under nitrogen flow, at 403 K for 8 h, to complete the reactions [15]. These products were named Nt, 2Nt and 3Nt. Fig. 1 shows a possibility for the reactions between thiocarbamide and all aminosilanes.

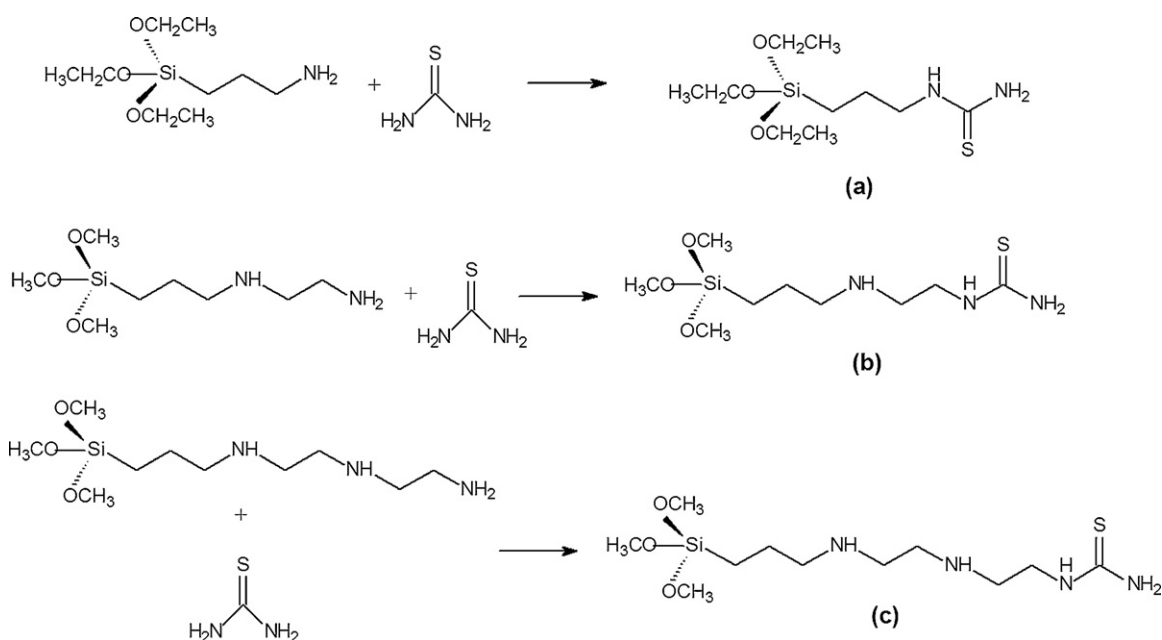


Fig. 1. Non-solvent reactions between the silanes N, 2N and 3N with thiocarbamide (t), giving the products Nt (a), 2Nt (b) and 3Nt (c), prior to SBA-15 incorporation.

Download English Version:

<https://daneshyari.com/en/article/1489493>

Download Persian Version:

<https://daneshyari.com/article/1489493>

[Daneshyari.com](https://daneshyari.com)