Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Surface Science 590 (2005) 51–62

SURFACE SCIENCE

www.elsevier.com/locate/susc

Interaction of divalent copper with two diaminealkyl hexagonal mesoporous silicas evaluated by adsorption and thermochemical data

José A.A. Sales [a], Alexandre G.S. Prado [b], Claudio Airoldi [a,*]

[a] Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, 13084-971 Campinas, São Paulo, Brazil
[b] Instituto de Química, Universidade de Brasília, Caixa Postal 4478, 70919-970 Brasília, Distrito Federal, Brazil

Received 22 November 2004; accepted for publication 6 June 2005

Abstract

Hexagonal mesoporous silicas chemically modified with ethylenediamine moieties were synthesized through the co-condensation of tetraethylorthosilicate (TEOS) with two different silylating agents: (i) *N*-[3-(trimethoxysilyl)propyl]-ethylenediamine and (ii) the new agent prepared from the incorporation of the ethylenediamine molecule into the epoxide group of the precursor 3-glycidoxypropyltrimethoxysilane. From these silylating agents under neutral *n*-octylamine template methodology, the respective MNN and MGNN inorganic–organic hybrids were synthesized. Elemental analysis showed that the number of pendant groups in these hybrids were 1.69 and 1.62 mmol g^{-1}, with pore diameters and surface areas of 1.81 and 1.53 nm and 663 ± 14 and 614 ± 16 $m^2\ g^{-1}$. Infrared spectroscopy, nuclear magnetic resonance for ^{13}C and ^{29}Si nuclei and X-ray diffraction patterns are in agreement with the success of the proposed synthetic methods, as confirmed for the formation of the mesoporous hybrids. Both mesoporous materials have been used for divalent copper adsorption from aqueous solution at 298 ± 1 K. The series of adsorption isotherms were adjusted to a modified Langmuir equation. The maximum number of moles adsorbed gave 1.4 ± 0.1 and 1.4 ± 0.2 mmol g^{-1} for MNN and MGNN, respectively. The same interactions were calorimetrically followed and gave exothermic enthalpy, negative Gibbs free energy and positive entropy values. These favorable thermodynamic data indicate cation/nitrogen basic center interactions on the new mesoporous materials at the liquid/solid interface for both systems.

Keywords: Silicon; Chemisorption; Solid–liquid interface; Porous solids; Coating; Surface thermodynamics; Compound formation

---

1. Introduction

The covalent immobilization of organic molecules with desired functions onto a variety

---

[*] Corresponding author. Tel.: +55 19 3788 3055; fax: +55 19 3788 3023.
E-mail address: airoldi@iqm.unicamp.br (C. Airoldi).

0039-6028/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2005.06.007

of inorganic surfaces can be designed in order to embrace characteristics having significant practical advantages, such as improved structural and thermal stability, swelling behavior, accessibility to the reactive centers, and insolubility in organic and aqueous solvents [1–8]. The development of new inorganic–organic hybrids with the ability to synthesize porous solid structures on nanometer scale, resulting in mesoporous silicates, which available pendant groups are useful to coordinate metal ions. This behavior provides a special approach in the green chemistry field as catalysis and for removal of contaminants [9–13]. Among many inorganic materials able to bind covalently organic compounds, silica gel is highly explored not only due to its abundance, high thermal and chemical stabilities, but also in considering its large surface area, and its associated properties [1,11–13]. However, a series of mesoporous silicate structures can be available by exploring reaction conditions with appropriated structure directors [14].

For synthesizing hybrids precursor silylating molecules are required, which must contain trialkoxy groups at one end of the organic chain in order to react with free silanol groups disposed on the silica gel surface or in a condition where the silanol groups can be formed during the course of the reaction. A successful methodology for this purpose is the employment of the sol–gel procedure [14]. This method consists basically in hydrolyzing a tetraethylalkoxysilane compound together the chosen silylating agent, in which the inorganic structure backbone formed has covalently attached organic moieties from the original silylating agent that contain the desired functional groups [15–17]. One of the most attractive uses of ligand grafted materials containing exposed amine groups is the ability to bind cations from diverse solutions [15,12,18].

Taking into account that the inorganic backbones can be well-structured when a template, such as a long neutral polar molecule dispersed in water as micelles is disposed, during the sol–gel process, a new material with highly order pores can be formed. For this purpose neutral amine surfactant micelles yielded as a mesostructure-directing agents offer additional advantages due to the facility in surfactant removal by solvent extraction procedure [19,20]. The novel materials then contain mesoporous structures loaded with pendant molecules on both the inner and outer pore surfaces of the solids, which display conditions to improve the adsorption characteristics of these materials [21,22].

The hybrids obtained from neutral templating methodology often present large textural pore volumes, which are also responsible for the enhanced catalytic performance and removal abilities for many materials [14,23–25]. The application of inorganic surfaces chemically modified with organic molecules for removal and pre-concentration of metal ions from solutions is of fundamental importance, especially in environmental studies [12,13,26–29]. Thus, the monitoring and removing of heavy metals in natural water are essential to indicate and reduce the possible effects of these contaminants on the normal life of a given community, due to the fact that the presence of high concentrations of heavy metals, mainly in water and foods, can cause many risks to mankind [8,30].

The purpose of this investigation was to develop a one-step process to prepare ligand grafted silica gel having available basic nitrogen atoms to act as chelating agents for complexing cations. To perform this objective a synthetic procedure was employed to obtain mesoporous materials, originating from ethylenediamine moieties, to adsorb divalent copper from aqueous solution. The reported synthetic diaminealkyl hexagonal mesoporous silicas are prepared from either a commercial precursor or from a newly prepared silylating agent.

2. Experimental

2.1. Chemicals

The silica source for the inorganic framework formation was derived from tetraethylorthosilane (TEOS). The silylating agents 3-glycidoxypropyltrimethoxysilane (Siepox), *N*-[3-(trimethoxysilyl)-propyl]-ethylenediamine (SiNN), the surfactant *n*-octylamine, ethylenediamine (en), methanol and ethanol were all reagent grade.