Microporous and Mesoporous Materials 276 (2019) 201–206

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

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

Vertically aligned porous silica thin films functionalized by nickel chloride incorporated in walls

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ARTICLE INFO

Keywords:
Mesoporous silica
Thin films
Functionalization
Functional materials
Raman spectroscopy
TEM
EPR

ABSTRACT

The article concerns a novel functional material in the form of thin film: vertically aligned mesoporous silica layer precisely functionalized by nickel chloride molecules. The functional units are placed exclusively inside silica walls, where they are chelated by cyclam (1,4,8,11-tetraazacyclotetradecane) molecules. The synthesis routes, based on a self-assembly approach, resulted in materials with the assumed molecular structure. The microscopic studies of the silica matrices structure confirmed that tetrasilylated cyclam did not perturb the formation of porous silica films. Vibrational spectroscopy showed incorporation of the cyclam inside silica structure. In turn, the EPR spectroscopy confirmed, that nickel dichloride was chelated by cyclam molecules, which resulted in a homogeneous distribution of functional nickel-containing groups.

1. Introduction

Nanotechnology for environmental engineering is a relatively new discipline which originated in the 1990s [1]. Since the inception of this field researchers have been working on the development of new materials, and on modifications of other products to improve their features [2]. However, one of the major challenges in the fabrication of the materials in the nanoscale (atomic or molecular) is the control of suitable and desirable physical or chemical properties of such materials. In this area, a bottom-up nanotechnology has opened opportunities for obtaining the materials with extraordinary features [3,4]. In particular, the host-guest systems are of essential importance in environmental engineering. Such materials are composed of the matrix and functional units distributed inside its volume. The matrix assures the suitable mechanical properties of the material providing a framework, while functional units are responsible for the chemical performance [5].

Mesoporous silica could be an ideal matrix for such materials. It has attracted interest since its discovery, in particular in its most popular forms of MCM 41 [6] and SBA-15 [7–9] which are important for applications. Both materials have cylindrical pores arranged with 6-fold symmetry within the crystalline (MCM 41) or amorphous (SBA-15) silica structure. Their advantages are homogenous pore distribution, large pore volume, and large specific area. Their strength is also the potential for functionalization [2]. The functional units can be distributed inside silica pores creating active material with a large specific area [10]. If such functional units are able to bind the harmful substances, we could fabricate an environmental filter (absorbent) with a large capacity. Such efforts have been already undertaken: for example the amino-functionalized mesoporous silica SBA-15 was applied for metal(II) removal [11,12], similarly to the silica functionalized by melamine-based dendrimers amine groups [13] or diaminocyclohexane grafted SBA-15 silica [14]. These results are promising and indicating there is indeed a need for further search for such novel materials for water or soil remediation. Importantly, these previous studies described mainly removal of metals(II), neglecting metals(I) and metals(III) which are abundant in the environment and also require removal. A potential solution to this problem could be the fabrication of multifunctional materials. However, in the case of some varieties of the porous silica functionalities, the pore volume are not large enough for to ascertain their correct distribution. Nonetheless, silica walls can also be used for the incorporation of the new functionalities. The best strategy, therefore, seems to be the functionalization of both silica pores and walls simultaneously: in such case, pore volume would remain available for bonding of other functional units.

Another concern is the form of the materials for environmental remediation. In most cases, the powders are used but thin films also have a great potential for applications: they can, for example, be used as coatings on dishes for water purification.

In the paper, we propose for the first time the thin film material based on porous silica matrix containing functional units placed

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https://doi.org/10.1016/j.micromeso.2018.10.002
Received 5 July 2018; Received in revised form 12 September 2018; Accepted 2 October 2018

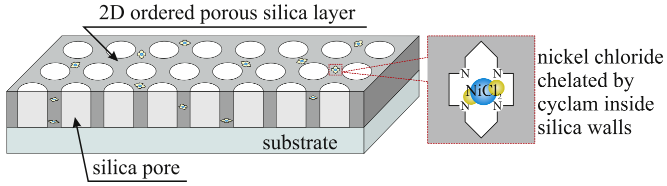

Fig. 1. Schematic representation of the vertically aligned porous thin silica film containing nickel chloride chelated by cyclam inside walls.

exclusively inside the silica walls. As a specimen possessing strongly chelating properties for metal(II) chlorides, we choose cyclam (1,4,8,11-tetraazacyclotetradecane). To check the concept and its applicative potential, we prepared the target material and reveal its molecular configuration after chelating nickel chloride molecules (as an example) by internal cyclam groups (hereafter called cyclam-$NiCl_2$). The concept could be validated by a successful formation of the vertically aligned porous thin silica film containing described functionalities inside walls, as shown in Fig. 1.

2. Materials and methods

2.1. Characterization methods

The thin films deposition was controlled by using a Biologic SP150 potentiostat. The reaction was carried out with the use of customized Teflon reactor.

In order to verify synthesis result and to determine the functional unit configuration, the thin films obtained were characterized by several methods. TEM imaging was carried out by applying the FEI Tecnai G2 20 X-TWIN electron microscope, equipped with emission source LaB6, CCD camera FEI Eagle 2 K. TEM images were processed with the help of the Gwyddion software [15].

The Raman spectra were recorded with the use of the WITec confocal Raman microscope CRM alpha 300 M equipped with an air-cooled solid-state laser ($\lambda = 532$ nm) and a CCD camera. The excitation laser radiation was coupled into a microscope through a single-mode optical fibre with a 50 mm diameter. An air Olympus MPLAN (100×/0.90NA) objective was used. Raman scattered light was focused onto a multi-mode fibre (50 mm of diameter) and monochromator with a 600 line/mm grating. The Raman spectra were accumulated by 30 scans with the integration time of 30 s and resolution of 3 cm^{-1}. The spectrometer monochromator was calibrated by using the Raman scattering line with a silicon plate (520.7 cm^{-1}). The spectra were collected at room temperature for the wavelength range of 100–4000 cm^{-1}. The baseline correction, cosmic ray removal and peak fitting analysis were performed with the help of GRAMS software package.

EPR measurements were carried out with the use of Bruker FT-EPR spectrometer ELEXSYS E580 continuous-wave X-band (9.850537 GHz). The spectra were recorded with microwave power in the range of 30–180 mW and using magnetic field modulation of about 5 G. EPR measurements at variable temperatures (50–300 K) were performed by using an Oxford Instruments cryostat. The samples were scratched off from the substrate and powdered before introduction into a capillary tube for EPR measurement. For spectra visualisation the EPRDataViewer software was used (freeware). The simulation of the EPR spectra and the evaluation of the EPR spectral parameters were carried out by applying commercial Bruker software (X-Sophe) [16]. We assumed a linear molecule of $NiCl_2$ to be a magnetic centre. For reproduction of the resonant line, we applied the powder-like spectrum with the spin Hamiltonian described by equation (1):

$$H = \beta\vec{B}\cdot\tilde{g}\cdot\vec{S} + \sum_i \vec{S}\cdot\tilde{A}_i\cdot\vec{I}_i \qquad (1)$$

where $\vec{B}$ is the magnetic field, $\tilde{g}$ represents the effective magnetic tensor, $\vec{S} = 1/2$ is the electronic spin operator for Ni^{3+} and $\tilde{A}_i$ represents the superhyperfine tensor with chlorine ions - for the main abundant isotope the nuclear spin $\vec{I_i} = 3/2$.

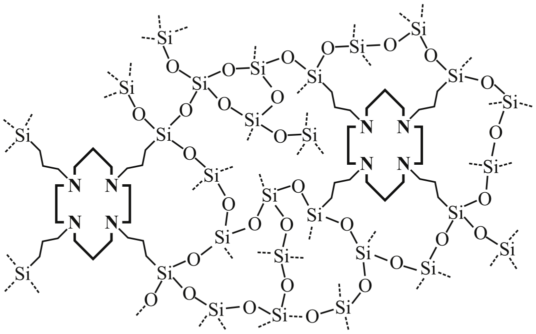

Fig. 2. Schematic representation of the cyclam molecules incorporated in the silica structure. Dotted lines represent the continuation of the structure.

2.2. Computational details

Density Functional Theory (DFT) simulations were carried out as a support for Raman spectroscopy. The simulations results allowed for correct identification the vibrational modes.

For this purpose, quantum-chemical simulations were performed to obtain a model, that could be used as a representative cluster model of a cyclam-nickel molecule built in the SBA-15 silica structure. During co-condensation of TS-cyclam with TEOS, cyclam molecules are encased by the silica and connected with SiO_2 groups via propyl chains, as shown in Fig. 2. The distance between cyclam groups, the length and the structure of SiO_2 depend on the molar proportion between TS-cyclam and TEOS used for the syntheses.

Designing and optimization of the exact model of such structure would not be feasible because the geometry optimization cannot be achieved in the finite time of calculations. We therefore prepared a simplified model of the cyclam incorporated in the silica structure. We approximated the silica structure by fragments of SiO_2 containing only 4 silicon atoms attached to cyclam-$NiCl_2$ molecule via propyl chains. We treated the SiO_2 part only as a ballast modifying the functional groups' vibrational modes. Since spectrum of the silica is well-known and was analysed thoroughly in our previous papers [17–19], we did not consider it here. The functional cyclam-$NiCl_2$ moiety was designed without simplification, as elements with unknown vibrational spectra.

Theoretical calculations were carried out in the gas phase with the use of the density functional theory (DFT) [20,21] available in the Gaussian 09 software package [22]. We applied two-stage geometry optimization. Firstly, the geometry of the model molecules was optimized by applying the Becke's hybrid exchange and correlated three-parameter [23] with the Lee-Yang-Parr correlation functional (B3LYP) [23–26] as well as the split-valence basis sets 3-21G. Afterwards, the initially optimized structures (a few conformers) were used as input files for further, more accurate, optimization. Here, we used the MOLPRO Basis Query def2-QZVP [27,28] as an accurate basis set which requires realistically achievable computational time. As a result of the geometry optimization, we obtained a few conformers for the model molecule. The final configuration of the model were selected on the basis of the conformational analysis – the conformer with the lowest energy was selected for further considerations. The obtained numerical model of a silica containing incorporated cyclam-$NiCl_2$ can be seen in Fig. 3.

The geometrically optimized structure was used as the input files for the vibrational harmonic calculations. For this purpose, we applied the same basis set as mentioned before (B3LYP/def2-QZVP). The structure obtained had positive harmonic vibrations which proved a true energy minimum [22]. The assignment of the calculated Raman bands was