



Metal-complex ionosilicas: Cationic mesoporous silica with Ni(II) and Cu(II) complexes in their framework

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ARTICLE INFO

Article history:

Received 1 October 2012

Accepted 8 December 2012

Available online 20 December 2012

Keywords:

Mesoporous silica

Hybrid materials

Co-condensation

Complexes immobilization

ABSTRACT

Metal-complex ionosilicas with cationic complexes into the mesoporous silica framework were prepared using anionic surfactants. The electrostatic interaction between the anionic surfactant and the cationic metal complexes incorporated in the silica framework allows for the fine tuning of the mesoporous structure. The gentle procedure of synthesis developed and mild ion-exchange extraction of the surfactant, allowed a cleaner route for the immobilization of homogeneous cationic catalysts in mesoporous silica, while protecting the structural and chemical integrity of the metal complexes.

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1. Introduction

The synthesis of periodic mesoporous organosilicas (PMO) based on the use of bridged organosilane precursors, $[(RO)_3Si-R'-Si(OR)_3]$, allows for the smart and homogeneous incorporation of organic moieties in a mesoporous inorganic matrix [1,2]. Inspired by this idea, we recently reported the preparation of mesoporous metal-complex silica materials using $[MCl_2(R'Si(OR)_3)]$ entities [3,4]. This synthetic route leads to hybrid materials in which the metal complex forms part of the silica framework in a similar manner that the organic moieties are part of PMO's [5]. Combining both bridged organosilanes and bridged metal-complex silanes, PMO materials with neutral Pd(II) complexes have been recently described elsewhere [6].

The main advantages of this approach are that it does not require organic co-solvents, anaerobic or anhydrous environments, and is carried out at mild conditions, preserving the integrity of the metal complexes in the frameworks. Besides our method, different cationic and neutral surfactant routes have been explored to incorporate neutral [7] and cationic [8] complexes into the framework of mesoporous materials. However, in all these cases, the incorporation of the complex into the inorganic framework takes place without interaction between the complex and the surfactant. Recently, El Hankari et al. [9] have reported the synthesis of nanostructured silica materials with ionic groups covalently

attached to the framework (*i*-silicas), by taking advantage of the ionic interaction between structure-directing agents (surfactant) and the organo-ionic part of the silica hybrid precursor. As many metal complexes are cationic, the present work describes, using a similar approach and for the first time, the incorporation of cationic complexes, Cu(II) and Ni(II)-complexes containing amine ligands, into the mesoporous silica framework using an anionic route.

In 2003, Tatsumi et al. [10(b)] reported the anionic surfactant templating route for synthesizing mesoporous silica materials (AMS). This approach was based on the co-structure-directing effect conducted for an aminosilane or quaternized aminosilane. The electrostatic interaction between the cationic head group of the 3-aminopropyltriethoxysilane or the quaternary ammonium group of the N-trimethoxysilylpropyl-N,N,N-trimethyl ammonium chloride (N^+) and the anionic surfactant (S^-), produces a uniform distribution of the organic groups in the pores of the material. This new route was designed as ' $S^- N^+ I^-$ pathway', where I^- represents the inorganic precursor. Since these first reports, many mesostructured materials have been successfully prepared by this method [11].

Surfactant extraction is a decisive step to retain the functional organic groups on the surface of the mesopores. Recently, Zheng et al. [12] developed a new and efficient method based on an ion-exchange process to remove anionic surfactants from AMS. Using highly concentrated salt solutions as extractants (X^+Y^-) it is possible to force the interaction of the anion with the positively charged protonated amino groups or quaternary ammonium groups (N^+), displacing the anionic surfactant (S^-) in the mesopores which would be released into the solution. This method could effectively remove the anionic surfactant while the complex structure is maintained.

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In this paper, we describe a new approach to synthesize mesoporous Cu(II) and Ni(II) complex silica materials based on anionic surfactant-assembly of cationic Cu(II) and Ni(II) complexes with trialkoxysilanes as terminal groups. The ion-exchange process used to remove the anionic surfactant allows its extraction with no damage for the complexes.

2. Experimental section

Synthesis: Cu(II) and Ni(II)-containing mesoporous materials were prepared using a facile one-pot method. In a typical synthesis, 0.11 g of anionic surfactant (sodium dodecyl sulfate (SDS), or sodium dodecanoate (SD)) (Aldrich, $\geq 99.0\%$) was dissolved in a water:ethanol mixture (24.3 g \cdot H₂O + 7.2 g EtOH) at 60 °C. Different quantities of the metal precursor (CuCl₂ or NiCl₂ \cdot 6H₂O, Aldrich) were then added to the solution. Once dissolved, a mixture of tetraethoxysilane (Aldrich, 98%) and the ligand used for the synthesis of the complexes, 3-aminopropyltriethoxysilane (APTS, Fluka $\geq 98.0\%$) were added dropwise. The molar composition of the synthesis gel was X APTS: (1–X) TEOS: 0.1 Surf.: 180H₂O: 20 EtOH, where X indicates the ratio of the ligand in the mixture TEOS/APTS, varied from 0.05 to 1. The final mixture was then reacted at 60 °C for 1 h under stirring (400 rpm), followed by aging at 60 °C for 24 h in a Teflon lined stainless steel autoclave. The obtained solid product was thoroughly washed (with water and ethanol), filtered off, and dried overnight at 40 °C. The surfactant was finally removed by the ion-exchange method. Typically, 0.10 g of the mesoporous material was treated with 20 ml of a concentrated solution of CH₃COONa, 1.04 M in a mixture H₂O:EtOH (30:70 v-v) during 12 h. Materials prepared with the Cu(II) complex were treated under reflux at 90 °C while Ni(II) complex had to be treated at RT to avoid damages in the complex.

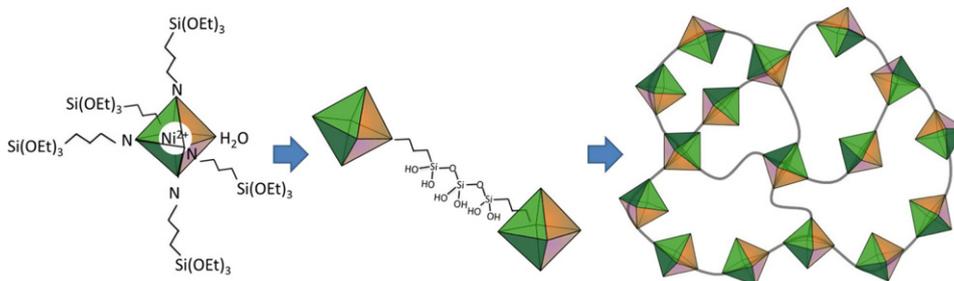
The molar ratio metal/ligand in the complexes was kept as 1/4 for the Cu(II) complex and 1/6 for the Ni(II) complex. Materials were denoted as X_{Cu}:4APTS(Surf) and X_{Ni}:6APTS(Surf), where

X/(1–X) is the molar ratio between the ligand and the TEOS and Surf is the anionic surfactant used (SDS or SD). A schematic representation of the preparation of mesoporous metal complex-silica materials is shown in Scheme 1.

3. Results and discussion

Mesoporous hybrid materials with homogeneous metal incorporation and good textural properties were obtained for Cu(II) complex materials with X=0.50 and for Ni(II) complex materials with X=0.25 and 0.50. Materials were obtained as blue solids, case of Cu(II) complex hybrid materials, and green solids, case of Ni(II) materials, as corresponding to the color of the starting complexes used in their synthesis. After removing the surfactant by ion-exchange with CH₃COONa solutions during 12 h at 90 °C or room temperature, the obtained materials kept their initial color, remaining the extraction solutions uncolored. Interestingly, in the case of the nickel complex materials, solids prepared only from the Ni(II) complex (X=1.0, without the addition of TEOS) were also obtained. This kind of materials will represent a new family of materials homologous to the PMOs but with a metallic complex bridge (instead of an organic one) between two inorganic moieties, i.e. O_{1.5}Si–R–M–R–SiO_{1.5}, where R represents an organic group, the ligand of the complex (–(CH₂)₃–NH₂, in this case) and M the metal of the complex (here, Ni(II)). The drawback of these new materials, i.e. solids from only metallic complexes, was the stability after the removal of the surfactant. The high amount of organic content with flexible aliphatic chains as ligands for the complexes, made the mesoporous structure not stable enough to resist the extraction of the surfactant and the mesoporous structure collapsed. TEM images of the as-synthesized solids, before the surfactant extraction, confirm the mesoporous nature of these novel materials, see Supporting information (SI1).

Table 1 shows the loading of metal into the mesoporous hybrid materials determined by ICP-OES. With regard to the initial



Scheme 1. Schematic representation of the experimental procedure. Ni(II) complex (left), silica-bonded metal complexes, and complex silica network.

Table 1
Textural parameters and metal incorporation in the mesoporous hybrid materials.

Metal	X ^a	Surf.	Metal ^b (wt%)	S _{BET} ^c (m ² g ⁻¹)	V _{meso} ^d (cm ³ g ⁻¹)	Ø _{meso} ^d (nm)
Cu(II)	0.50	SD	8.60 (8.70 ^e)	350	0.40	2.1
		SDS	8.20 (8.70 ^e)	410	0.55	2.6
Ni(II)	0.25	SD	2.49 (3.37 ^e)	230	0.20	2.5
		SDS	1.70 (3.37 ^e)	220	0.29	2.7
	0.50	SD	4.80 (5.55 ^e)	280	0.25	2.2
		SDS	4.20 (5.55 ^e)	320	0.40	3.0

^a Molar ratio of the ligand APTS with respect to the TEOS, X APTES: (1–X) TEOS.

^b Calculated by ICP-OES analysis of the filtrate after treatment of the samples with *aqua regia*.

^c BET surface area estimated by using multipoint BET method using the adsorption data in the relative pressure (P/P₀) range of 0.05–0.30.

^d Mesopore volume and average pore diameter calculated from the adsorption branch according to the BJH method.

^e Theoretical values.

amount of Cu(II) or Ni(II) in the synthetic gel, metals were incorporated with good yields into the material, being > 50% of the theoretical amount in any case. The incorporation is almost quantitative in the case of the most stable complex, Cu(II), while for Ni(II) complex it improves when the nominal metal loading

increases. Metal loading as high as 8.60 wt% Cu(II):material and 4.80 wt% Ni(II):material can be easily obtained with this facile one-step method, avoiding the use of any other organic co-solvent and making the synthesis more environmentally friendly with regard to typical post-synthetic methods (grafting).

The coordination state of the Ni(II) and Cu(II) ions after their incorporation into the materials was confirmed by diffuse reflectance UV–visible spectroscopy (DRUV); for comparison purposes UV spectra of $[M(H_2O)_x]^{2+}$ and $[M(NH_3)_x]^{2+}$ were also collected. Cu(II) complexes with squared planar structure usually show a unique band in the visible region of the spectrum [13]. Mesoporous hybrid materials with Cu(II) complexes in their structures show only a band at 680 nm (see Fig. 1(a)), suggesting the squared planar coordination of Cu(II) ions in these solids. The small red shift of the band in comparison with the Tetraamminecopper(II) complex in solution, $[Cu(NH_3)_4]^{2+}$ (625 nm) and the big difference between the positions of the peak with the hydrated complex ($[Cu(H_2O)_4]^{2+}$, 810 nm), suggest that not substitution of the amine ligands by water molecules takes place during the experimental procedure and the complex is mostly incorporated as $[Cu(APTS)_4]^{2+}$ specie.

Materials obtained from the Ni(II) complex present a more complicated spectrum. Three bands are visible in the DRUV spectra of the Ni(II) hybrid materials (see SI2) at 387 nm, 700 nm and 1100 nm, as correspond to octahedral configurations in Ni(II) complexes [14]. In this case, the hydration of the complex is determined by the shift of the peak around 400 nm to lower energy regions (see Fig. 1(b)). The position of this band in complexes with aliphatic amines (propylamine in our case) has been reported at 370 nm [14(c)]. In the hybrid materials, the displacement of this band at 387 nm (near to the band of the totally hydrated complex, $[Ni(H_2O)_6]^{2+}$, 395 nm) suggests the replacement of amino ligands by water molecules, being the dominant specie incorporated to the silica a hydrated specie $[Ni(H_2O)_{6-x}(APTS)_x]^{2+}$.

The mesoporous nature of the hybrid materials was investigated by TEM (SI3) and N_2 adsorption/desorption isotherms, Fig. 2. In any case, the mesostructures consist mostly of highly homogeneous interconnected spherical particles which are about 100–300 nm. Materials exhibit a non-ordered wormhole-like system of small size mesopores. All materials show type IV isotherms with regular BET surface areas (200–400 $m^2 g^{-1}$) and total pore volumes (0.20–0.55 $cm^3 g^{-1}$), and small average pore diameters (2–3 nm), see Table 1. The high loading of metal complexes in the hybrid materials, 4.80 wt% Ni(II) and 8.60 wt% Cu(II), and the location of the complexes into the mesoporous surface area, can explain the lower BET surface area and pore volume regarding other materials synthesized by the anionic route [10–11].

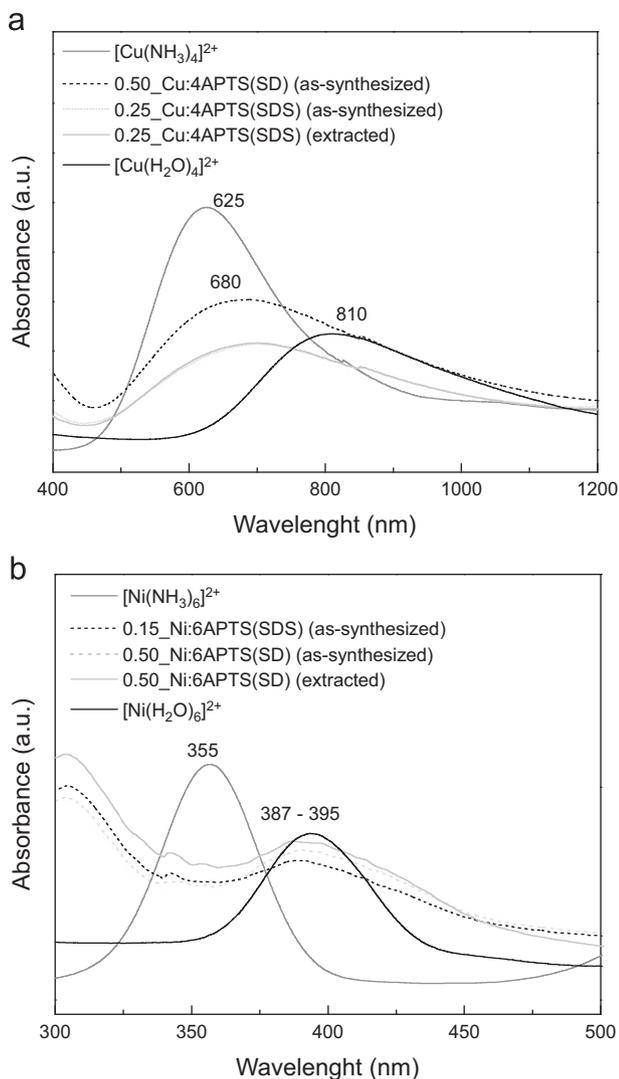


Fig. 1. DRUV spectra of mesoporous materials with the (a) Cu(II) complex and (b) Ni(II) complex in their structure.

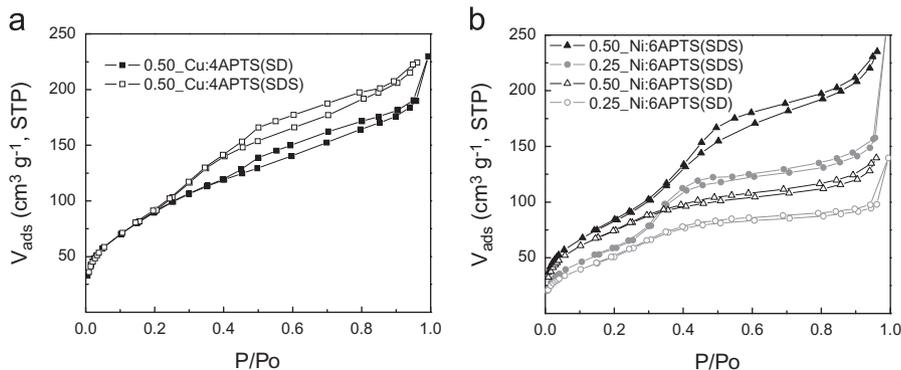


Fig. 2. N_2 adsorption/desorption isotherms of materials prepared from (a) the Cu(II) complex and (b) the Ni(II) complex.

4. Conclusions

In conclusion, we have reported a new and efficient methodology for the synthesis of mesoporous silica materials with cationic complexes into the framework of the material. The anionic route allows a quantitative incorporation of the metal complex into the structure, which consist of wormhole like mesoporous particles with good textural properties. High metal contents, 8.60 wt% Cu(II) and 4.80 wt% Ni(II), with good BET surface areas ($300\text{--}400\text{ m}^2\text{ g}^{-1}$) can be easily reached in a one-pot, direct synthesis. The incorporation method is general and should also serve to incorporate other cationic metal complexes in hybrid silica matrices.

Acknowledgments

The authors are grateful for funding under project CTQ2011-28954-C02-01(02) from the Spanish MICINN. E.S. is grateful for financial support under the JdC Program (Ref. JCI 2008-2165) and from GV (Ref. BEST2011/223). NL acknowledges financial support from the FPI Program (Ref. BES-2006-13056).

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