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Surfactant-templated silica doped with 1-phenyl-3-methyl-4-stearoylpyrazol-5-one (HPMSP) as a new sorbent

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A new sorbent for transition elements was prepared in a one-step synthesis by encapsulation of a pyrazolone ligand in a surfactant-templated silica. This new material was characterized by X-ray diffraction (XRD), nitrogen physisorption and transmission electron microscopy (TEM). The material presents a lamellar symmetry with a pore diameter of 39 Å. The use of a cationic surfactant allows a high loading of ligand (0.43 mol kg^{-1}), associated with complete accessibility of the ligand to the aqueous phase. A sorption capacity of 0.2 mol kg^{-1} was observed for copper ions in a $NaNO_3$ 0.01 M medium. Complete elution of copper species is possible with HNO_3 1 M.

Introduction

Modern analytical detectors are offering lower and lower detection limits. They are however expensive and not always robust and, in spite of their sensitivity, a purification and/or preconcentration step has to be added for the analysis of complex matrices (*e.g.* environmental and biological samples). Liquid–liquid extraction has been used for several years and is still in use, but the use of organic solvents, often toxic, and the fact that on-line detection is not possible, has led to the development of solid-phase extraction procedures.

However, the sorbents available for inorganic trace element analysis are not very selective and the presence of a high content of interfering ions generally prevents the selective preconcentration of trace elements. To increase the selectivity of the support, impregnation or chemical derivatization with a chemical reagent is currently used.[1] The support is generally either polymeric, *e.g.* polystyrene–divinylbenzene resins, or inorganic *e.g.* silica. Inorganic supports combine several advantages over comparable functional polymers: resistance to mechanical deformation, hydrophilic properties, negligible swelling and chemical inertness in spite of their solubility at high pH. These advantages explain the popularity of the C_{18} bonded silica phases largely employed in reversed phase chromatography. However, chemical bonding on silica of reagents other than the traditional alkyl groups generally requires several synthesis steps and has to be tailored for each organic reagent. Moreover, the complexing reagents which can be bound to the silica are limited. With the impregnation technique, the reagent is physically adsorbed on the porous material. The technology is highly versatile and a large variety of reagents have already been loaded on silica. However, the binding force is quite low in this case and leaching is currently observed, limiting the lifetime of the support.

Another route for immobilizing reagents is the direct encapsulation of a molecule by using sol–gel technology. In this case, the synthesis of silica is carried out in solution and at low temperature, which allows the introduction of the organic complexant in a mixture of sol–gel precursors. Several authors have already used this technique to prepare colorimetric or pHmetric sensors because of its high versatility in the choice of the molecules.[2–5]

In addition, the pore size of silica is particularly crucial for preconcentration applications because this parameter controls the kinetics of the exchanges. The use of surfactants in a micellar arrangement has led to ordered mesoporous (MCM-41 type) silicas with pores organized in lamellar, cubic or hexagonal structures.[6,7] Thanks to this organization, the material has not only a low tortuosity but also a large specific surface. One of the first applications for these materials was catalytic cracking of large molecules. But their higher surface areas are also very attractive for adsorption applications and some authors have already functionalized them by impregnation or grafting techniques. Dye-doped photosensitive mesostructured materials have been prepared with chlorophyll and phthalocyanine involving a co-organizing process of the surfactant and dyes.[8] But to our knowledge, no surfactant-templated silica doped for separation applications has been described to date.

In this work, we describe the encapsulation of 1-phenyl-3-methyl-4-stearoylpyrazol-5-one (HPMSP) in silica prepared *via* a micellar route. Chelating properties of HPMSP with respect to the transition elements and certain heavy metals have been largely studied in liquid–liquid extraction.[9–12]

The resulting material was characterized by porosimetry measurements, transmission electron microscopy, IR spectroscopy and X-ray diffraction. The adsorption of copper was studied with respect to pH conditions, and elution conditions have been determined.

Experimental

Reagents

Tetraethoxysilane (TEOS, 98%) was purchased from Aldrich, methanol (CH_3OH, 99.9%) was from Carlo Erba and cetyltrimethylammonium bromide (CTAB, 99%) was obtained from Acros. Copper solutions were prepared from analytical grade nitrates and deionised water (MilliQ RG, Millipore) was used throughout.

1-phenyl-3-methyl-4-stearoylpyrazol-5-ol (HPMSP) was synthesized according to Jensen.[13]

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Synthesis

The synthesis procedure was directly inspired from Firouzi *et al.*[14] CTAB is dissolved in an aqueous solution of NaOH 0.1 M under vigorous stirring and maintained at 60 °C. Methanol is then added. The extracting molecule (HPMSP) is next introduced into the mixture, still under stirring. After its dissolution, TEOS is added. The final molar composition of the solution is 1 TEOS : 140 H_2O : 13 CH_3OH : 0.18 CTAB : 0.0625 HPMSP. A few minutes after the addition of TEOS, silica precipitation is observed. The stirring is maintained at ambient temperature during 24 hours then the yellowish precipitate is filtered, washed copiously with water until neutral pH and dried in an oven at 60 °C overnight. The product is placed under vacuum at 60 °C for 24 hours more.

A control silica that did not contain the HPMSP ligand was prepared to be used as a blank.

Apparatus

The nitrogen adsorption isotherm was measured on a Sorptomatic 1990 instrument following calcination of the sample at 500 °C during one night and out-gassing at 300 °C under vacuum for 3 hours. The transmission electron microscope (TEM) used was a TOPCON 002B working at 200 kV. The sample is first dispersed in alcohol and deposited on a copper grid provided with a carbon membrane.

X-Ray diffraction was performed on a Siemens D5000 (Cu-$K_{\alpha 1}$ radiation, λ = 1.5406 Å) and UV spectra were obtained on a HP 8453 UV-Visible spectrometer. The FTIR spectra were recorded on a Nicolet 5DXC spectrometer using KBr pellet techniques. Metal ion contents of extraction solutions were measured on a Perkin Elmer 2380 Atomic Absorption Spectrometer.

Cu^{2+} extraction/leaching experiments

All experiments were performed at 25 °C in thermoregulated baths.

Freshly conditioned material (200 mg) was soaked in 25 mL of a 200 ppm $Cu(NO_3)_2$ solution in HNO_3 0.01 M for 24 hours. The liquid was separated from the solid by centrifugation at 12 000 rpm and the final pH and copper content of the supernatant was measured.

Results and discussion

Conformation of HPMSP in silica

The FTIR spectra of HPMSP, CTAB and doped silica are shown in Fig. 1.

The FTIR spectrum of HPMSP shows the usual bands for this molecule[15–17] that presents several tautomeric forms (see Fig. 2). In the region of C=O stretching vibrations, there are 3 bands at 1626 cm^{-1}, 1598 cm^{-1} and 1558 cm^{-1}. The first one at 1626 cm^{-1} is attributed to an intramolecular chelated C=O of the enol form. The second band at 1598 cm^{-1} is attributed to the benzene ring. Finally, the third band at 1558 cm^{-1} is attributed to the chelated C=C bond of the enol form.

The FTIR spectrum of the doped silica shows the characteristic bands of the silica framework (Si-O-Si at 1090 cm^{-1} and 800 cm^{-1}; Si-OH at 970 cm^{-1}) as well as the CH bands of CTAB and HPMSP (2920 cm^{-1} and 2850 cm^{-1}). But only two characteristic bands of the pyrazolone group are present: C=O bands at 1644 cm^{-1} and at 1598 cm^{-1} (phenyl ring). The absence of the third band at 1558 cm^{-1} may be explained as follows: a) HPMSP is in keto–enolic form but the formation of an intramolecular chelate is not possible; intermolecular H bonds may be formed with water molecules included in silica; b) an ion pair $PMSP^-$–CTA^+ is formed in the silica which also prevents the formation of an intramolecular chelate; c) HPMSP is in the ketone conformation in silica.

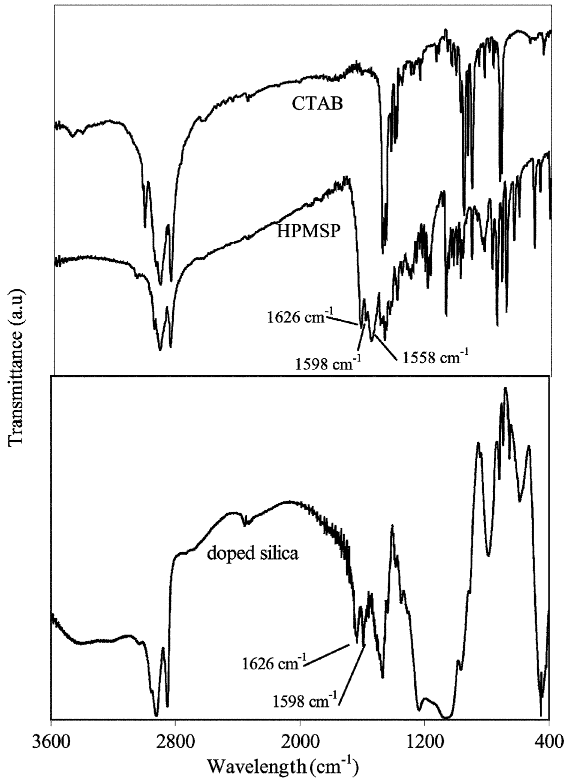

Fig. 1 IR spectra (KBr pellets) of CTAB, HPMSP and doped silica.

Loading in ligand

The quantity of ligand incorporated per mass of material is a significant characteristic for a specific support intended for use in preconcentration because it determines its exchange capacity. A UV spectrum, carried out on the filtrate of the synthesis solution, has shown that the filtrate of the synthesis mixture does not contain the chelating molecule. On the contrary, the surfactant is present as indicated by the foam formed during filtration. So, it means that the ligand is entirely incorporated in the silica framework but that only a part of the surfactant is entrapped. Nevertheless, the quantity of entrapped CTAB is not known and is perhaps variable from one synthesis to another. In addition, the final mass of material cannot be determined with precision because part of the solid is lost during the synthesis. The exact proportion of HPMSP cannot thus be calculated directly. To evaluate this content, the loss of mass from 120 °C to 500 °C was measured on five materials resulting from different syntheses. This value represents the organic matter plus the residual water content of the materials that have been dried at 60 °C under vacuum. Considering that the calcinated material is made up of silica only and that the Si : HPMSP was preserved, the final mass gives access to the content of HPMSP in the composite

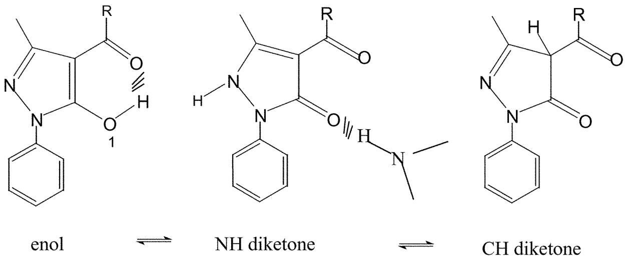

Fig. 2 Possible tautomers of 4-acylpyrazol-5-ones.

materials. The content of organic compounds appears very significant since it accounts for almost 60% of the material. Finally, the content of HPMSP is about 0.43 mol kg^{-1}. Furthermore, the reproducibility of the CTAB entrapping, and as a consequence the reproducibility of the synthesis, appears rather good since the standard deviation measured for this content in the five materials prepared is about 1%.

In order to confirm the content of HPMSP determined by gravimetry, the content of a heptane–ethyl alcohol (1 : 1) solution added to the material was determined by UV spectrometry after centrifugation. In general, the content obtained in this way is a little bit higher (0.45 mol kg^{-1}) than the result obtained by gravimetry. This means that the ligand is extracted quantitatively with this solvent and so, the accessibility of the molecule to the liquid is excellent. The worst reproducibility observed (RSD = 7%) is perhaps due more to a lack of reproducibility of the extraction than to a lack of reproducibility of the synthesis. It should be noted that water and heptane taken separately were also tested for the extraction of HPMSP but none of these solvents taken separately allows the leaching of the ligand. We can conclude from these observations that the doped silica is rather hydrophilic in spite of the presence of CTAB since ethanol is necessary to adjust the polarity of heptane to a value that allows its entrance inside the network. The material obtained thus combines great accessibility of the organic ligand to the aqueous phase and properties of hydrophilicity that are always appreciated to ensure a good affinity with aqueous solutions. On the other hand, the use of this support is not recommended in the presence of mixtures of solvent.

Morphological characteristics

The specific surface of the blank and doped silica with the pores filled with surfactant and ligand is about 20 m^2 g^{-1}. To release the porous structure, it is necessary to calcinate the sample overnight at 500 °C. The specific area of the blank is then 1200 m^2 g^{-1} and its isotherm is of type IV. The specific surface of the doped silica is a little lower with a value of 960 m^2 g^{-1}. The introduction of the ligand leads to a modification of the isotherm that presents an important H4 hysteresis (see Fig. 3), characteristic of slit-shaped pores. HPMSP addition increases the pore diameter from 24 Å to 39 Å as shown in Fig. 3 and the pore volume from 1.41 cm^3 g^{-1} to 1.83 cm^3 g^{-1}.

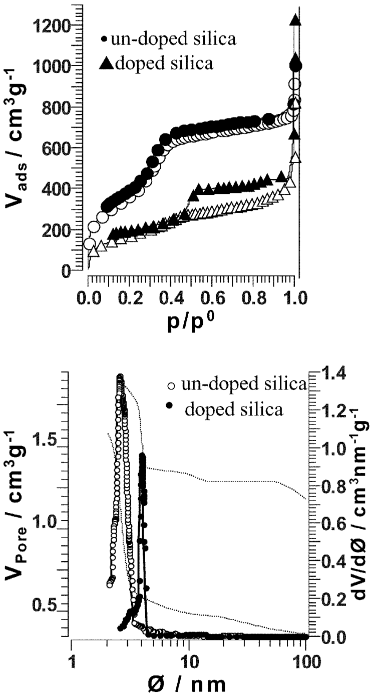

Fig. 3 Nitrogen adsorption–desorption isotherms (○ adsorption branch; ● desorption branch) and pore size distribution (ø = pore diameter) of undoped and doped silica.

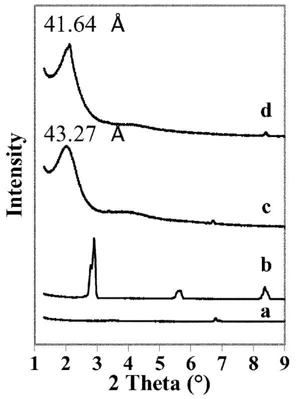

Fig. 4 X-Ray diffraction patterns of CTAB (a), HPMSP (b), undoped silica (c) and doped silica (d).

Similar isotherms have been observed when decane is used as an expander[18] and also when silica is prepared using a neutral diamine bolaamphiphile.[19] TEM images have revealed the presence of crystals with a sandy rose like structure in the first case and the presence of multilamellar vesicles in the second case. In the as-synthesized doped material of this work, TEM shows many organized parts that seem to have the same lamellar structures. The lamellar formations can be curved or straight fibers and the dimensions of the organized parts appear rather small. Cai *et al.*[20] have suggested that the use of a concentrated solution of CTAB during the synthesis, as is the case in our work, can give a high nucleation rate and lead to a supersaturation growth resulting in short range order.

The XRD diagram of the as-synthesized material (Fig. 4) presents a diffraction peak which disappears by calcination, which we are certain is because the curved formations have been ruffled by this treatment. The diffraction angle observed with the as-synthesized material corresponds to an interplanar distance of 41.6 Å. This value can not be directly compared to the pore diameter obtained with the desorption isotherm that was measured for calcinated samples. Indeed, the calcination step usually decreases the pore diameter.

Cu^{2+} adsorption

At first, no adsorption was observed on undoped freshly prepared silicas, but a weak adsorption was observed on silicas prepared several months earlier. It is probable that quaternary ammonium is transformed into amine with time, following the Hoffman degradation observed with ion-exchange resins.[21] If degradation continues to the formation of the secondary amine, this can then form a complex with copper. Further experiments were always carried out using freshly prepared doped silicas.

The first experiment was carried out by placing doped silica in an aqueous solution of copper. The silica color immediately changed to green which is characteristic of a Cu–HPMSP complex. The solution, analyzed by AAS, no longer contained Cu which means that the extraction is complete or that Cu precipitates as $Cu(OH)_2$. Indeed, the pH measured in the solution is about 6 and $Cu(OH)_2$ precipitation occurs above pH 5.

Further experiments were consequently carried out using copper solutions diluted in HNO_3 0.01 M. In these conditions, the capacity of doped silica reached 0.15 mol kg^{-1} of dry weight for copper and the equilibrium pH is 2.3. Addition of $NaNO_3$ 0.1 M increased this capacity significantly up to 0.2 mol kg^{-1}. This improvement may be explained by better separation of the solid particles whose dimensions are in the colloidal range. Indeed, without salt, we observe some particles in suspension even after a centrifugation of long duration. Quaternary ammonium adsorbed at the surface of particles can create a positively charged surface that repulses the other colloids, preventing them from precipitation. This positive layer could also repulse some of the cationic copper species, decreasing the capacity.

This behavior observed in the presence of a salt is particularly interesting because the material will be adapted to applications in ion separation from a charged matrix.

If one considers the ligand loading measured previously (0.43 mol kg^{-1}), one notes that the Cu : ligand ratio is almost 0.5. However, during the experiments carried out in liquid–liquid extraction, the complex formed between HPMSP and copper has a 2 : 1 stoichiometry. If the complex keeps this stoichiometry in the solid support, then all of the ligand is engaged in the complexation of metal and thus, the ligand is entirely accessible for the complexation of copper. The measured capacity can be compared to the capacity of silica (Aerosil 200) impregnated by the same ligand. For copper, Tong and co-workers[22] measured an adsorption capacity of 0.43 mmol kg^{-1}. The capacity of the doped silica is approximately 500 times larger than that of the impregnated silica.

The adsorption kinetics is quite fast since half of the capacity is reached within 4 minutes. This high speed of exchange can be explained at the same time by the low grain size and by the great accessibility of the ligand to the aqueous solution.

Maximum retention is reached at a pH value above 1, two units lower than in liquid–liquid extraction. This low pH value indicates strong complexation of HPMSP with copper and should be compared to the pK_a value of the ligand that is known to be around 4.1.

As a consequence of the great stability of the complex, a 1 M HNO_3 solution is required to release the copper quantitatively from the doped silica within 5 minutes.

Conclusion

The current work has shown that the functionalization of a templated-surfactant silica was possible by the doping technique with great ease. This route of synthesis offers a high accessibility of the encapsulated ligand to ions present in the aqueous phase and allows high loading levels of ligands to be reached. That is why the silica doped with HPMSP has shown excellent capacity for copper ions associated with an interesting kinetics of adsorption. Tests of recyclability of the doped silicas have still to be performed but we have demonstrated the possibility of complete elution of the metal adsorbed. These results are promising for encapsulation of a large variety of specific ligands in silica with a fast and simple synthesis.

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