

Synthesis and Characterization of Novel Porous SiO₂ Material Functionalized with C,C-Pyridylpyrazole Receptor

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ABSTRACT: A simple heterogeneous synthesis of pure modified porous polysiloxane SiO₂ by condensing a functionalized C,C-pyridylpyrazole with a 3-glycidoxy-propyl-trimethoxy-silane silylant agent, previously anchored on a silica surface is reported. The epoxide group was opened yielding a receptor pendant group bonded to the inorganic surface. The surface modification (MS) was characterized by elemental analysis, infrared spectra, nitrogen

adsorption–desorption isotherm, BET surface area and B.J.H. Pore sizes. The new material exhibits good chemical and thermal stability determined by thermogravimetry curves. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 3345–3349, 2010

Key words: porous material; pore size; surface area; thermal stability

INTRODUCTION

Porous materials have been widely used in applications, such as concentration and separation processes,^{1–4} ion exchange,⁵ chemical sensors,^{6–8} heterogeneous catalysis,⁹ biotechnology,¹⁰ electrochemistry,⁷ molten metal filtration,¹¹ yeasts fixation,¹² hot gas filtration,^{13–15} isolation and concentration of target analytes, and the clean-up of samples (removal of matrix interferences) in pharmaceutical, clinical, environmental and food chemistry.¹⁶ To meet the stringent requirements of these applications, it is essential for control purposes that the porous materials be characterizable and the determination of porosity, pore volume, pore size, specific surface area, thermal stability are among the most fundamental properties of porous materials.

The main advantages of these required porous materials are because of their: (i) higher enrichment factors; (ii) safety with respect to hazardous samples; and (iii) minimal costs because of low consumption of reagents.

Recently, the use of organic–inorganic materials, such as SiO₂, Al₂O₃, and TiO₂ has been interesting in the research.^{17–25} First, immobilized receptor on the inorganic support can liberate the organic guest molecule into the solution containing the pollutant.

Second, the organic–inorganic hybrid materials can be recyclable by suitable chemical treatment. Lastly, functionalized organic–inorganic materials display high selective and absorption changes because of their large surface area and well-defined pores in comparison to spherical structures. So, taking advantage of the homogeneous porosity with the large surface area, the porous silica, regarded as a polymer of silicic acid, has been quite interesting as an inorganic support.^{26–34}

Porous polysiloxanes SiO₂ (silicas) with high specific surface and adjustable pore have gained renewed interest as a class of products presenting some particular characteristics when modified with selected organic groups. It is not surprising, therefore, to note that the chemistry of the interior surface of polysiloxane plays a dominant role in its chemical and physical behavior. It is this property that makes silica gel an attractive material for use as catalysts, catalyst substrates, and adsorbents.

Although unmodified porous silicas show no specific interactions with metal ions, organo-functionalization may be used to make them suitable for metal ions complexation. Indeed, porous polysiloxane-immobilized ligand systems showed strong complexing properties in presence of some heavy metals.

To this end, we report in this article our preliminary results for the preparation and the characterization of a new organic–inorganic material (MS) (Fig. 1) obtained by grafting of functionalized receptor on porous silica, based on a recent³⁵ synthesized C,C-pyridylpyrazole. The immobilization of this

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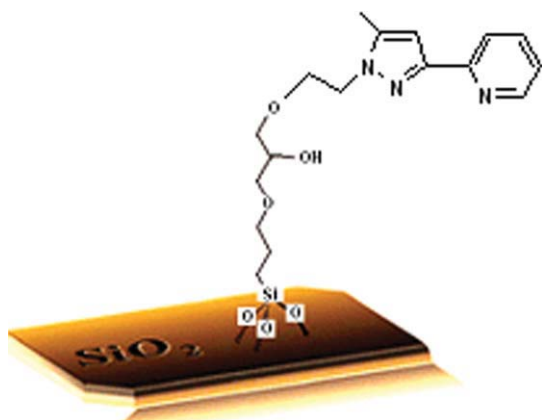


Figure 1 Modified SiO₂ with *C,C*-pyridylpyrazole receptor. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

receptor on silica gel was carried out through an arm spacer rather long in order to facilitate the contact between the receiver and the hazardous samples, it is about the arm 3-glycidoxypropyltrimethoxysilane which was used recently as silylating agent in the immobilization of many structures on silica gel.^{36,37}

EXPERIMENTAL

All solvents and others chemicals purchased from commercial sources were of analytical grade and used without further purification. Silica gel (E. Merck) with particle size in the range 70–230 mesh, median pore diameter 60 Å, was activated before use by heating at 160°C during 24 h. The silylating agent 3-glycidoxypropyltrimethoxysilane (Janssen Chimica) was used without purification. *C,C*-pyridylpyrazole was prepared as reported in our previous works.³⁵ Infrared spectra were obtained with Perkin–Elmer 1310. The product was analyzed by elemental analysis on a Perkin–Elmer PE-2400 elemental analyzer. A specific area of modified silica was determined by using the BET equation. The nitrogen adsorption–desorption isotherms were obtained by means of a Thermoquest Sorpsomatic1990 analyzer, after the material had been purged in a stream of dry nitrogen. The mass loss determinations were performed under (90% of oxygen and 10% of nitrogen) on a TGA Q50 V6.7 Build 203 instrument, at a heating rate of 10°C min⁻¹.

Immobilization of *C,C*-pyridylpyrazole compound on silica gel surface

The procedure for the preparation of a new material was adopted from the literature,³⁸ and was used without any other treatment. In a typical preparation, the converted hydroxy-substituted *C,C*-pyridyl-

pyrazole³⁵ to the alcoholate derivative using sodium metal in tetrahydrofuran was added to a suspension of epoxy-substituted silica (10 g) in 300 mL of dimethylformamide (DMF). The mixture was stirred and refluxed under nitrogen for 24 h. The solid material was filtered and the residue was washed with DMF, toluene, water (distilled and deionized), methanol, dichloromethane (150 mL of each) and finally dried.

Determination of the *C,C*-pyridylpyrazole groups

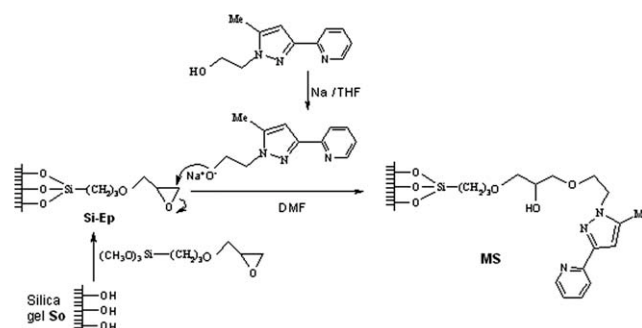
The amount of *C,C*-pyridylpyrazole groups grafted on epoxy-silica was determined by four different methods: (i) elemental analysis of nitrogen; (ii) from the determination of the unreacted epoxy groups by thiosulfate method;^{39–41} 3-Glycidoxypropyl-functionalized silica (MS) (200 × 10⁻³ g) was vigorously shaken with 10 mL of sodium thiosulfate (6 × 10⁻³M) to constant pH and the released hydroxyl groups were titrated with hydrochloric acid (0.1M); (iii) determination of the mass loss by thermogravimetry curves; and (iv) by simple weight measurement of the quantity of material before and after grafting on epoxy-silica.

RESULTS AND DISCUSSION

Preparation of the material

The synthetic procedure to describe the new material can be summarized in Scheme 1. The first stage of the preparation consists in reacting the activated silica gel with 3-glycidoxypropyltrimethoxysilane to form the epoxy-silica³⁸ that acts as precursor for further immobilization of the molecule containing the donor atom. The second stage involved the condensation of the *C,C*-pyridylpyrazole³⁵ salt with epoxy-silica to give the target material MS as shown in Scheme 1.

The results of the determination of the amount of *C,C*-pyridylpyrazole groups determined in four ways gave concordant results (Table I) at 280 μmol g⁻¹ of *C,C*-pyridylpyrazole groups per gram of silica.



Scheme 1 Synthetic procedure of modified SiO₂.

TABLE I
Determination of the C,C-Pyridylpyrazole Groups Per Gram of Support

	C,C-pyridylpyrazole groups ($\mu\text{mol g}^{-1}$) of support
Elemental analysis of nitrogen	280
Thiosulfate method	281
Thermogravimetry method	280
Weighing method	278

Infrared characterization of the material

The infrared spectra (Fig. 2) of the modified silica MS shows the strong decrease of the large $\nu(\text{OH})$ adsorption around 3300 cm^{-1} and the appearance of a $\nu(\text{C-H})$ weak band at $3000\text{--}2800\text{ cm}^{-1}$ corresponding to the organic receptor attached to the inorganic matrix. Another characteristic band $\nu(\text{Si-OH})$ assigned to silanol groups was observed near 965 cm^{-1} for the activated silica. After immobilization of the organic groups, this band was considerably reduced as expected in such immobilization processes.³⁷ In addition to those bands the modified silica, displays the characteristic C=N and C=C stretching vibrations at 1637 and 1491 cm^{-1} , respectively.

Surface characterization

Figure 3 shows the nitrogen adsorption-desorption isotherm of a sample at the various relative pressure (P/P_0). The isotherm is of Type IV according to the I.U.P.A.C. classification^{42,43} and displays a pronounced hysteresis for partial pressures $0.4 < P/P_0 < 1$, which is the direct evidence of the presence of mesopores.^{42,43} In addition, the hysteresis loops is of Type H2 which indicates that there is a uniform pore diameter distribution.

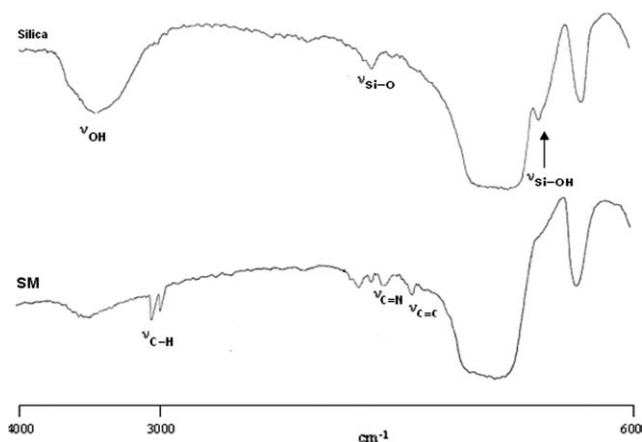


Figure 2 Infrared spectra of porous silica and modified silica MS.

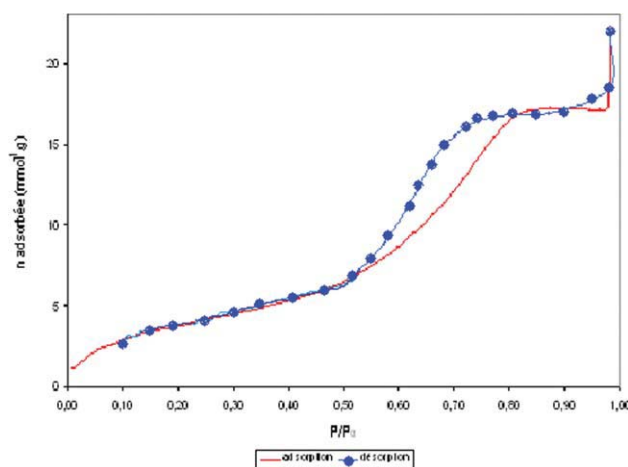


Figure 3 Nitrogen adsorption-desorption isotherm plots of sample. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The density of the pendant groups covalently attached to the inorganic silica backbone changes the original characteristic of the surface. Thus, the initial specific surface area of $550\text{ m}^2\text{ g}^{-1}$ decreases as the immobilization takes place to give $314\text{ m}^2\text{ g}^{-1}$ determined through the BET line (Brunauer-Emmett-Teller) (Fig. 4). The pore volume and the pore diameter of MS determined by nitrogen adsorption-desorption isotherms (Fig. 3) and Barrett-Joyner-Halenda (BJH) pore sizes (Fig. 5) decrease also to give $0.690\text{ cm}^3\text{ g}^{-1}$ and 2.866 nm , respectively (Table II).

The decreased parameters are attributable to the presence of the grafted receptor on the silica surface that partially blocks the adsorption of nitrogen molecules. In addition, the median pore size distribution of 2.866 nm provides the evidence for the uniform framework porosity of the material⁴⁴ and confirms the presence of mesopores. Figure 4 leads also to a decrease of the monolayer capacity of $N_m = 71.96\text{ cm}^3\text{ g}^{-1}$ used to

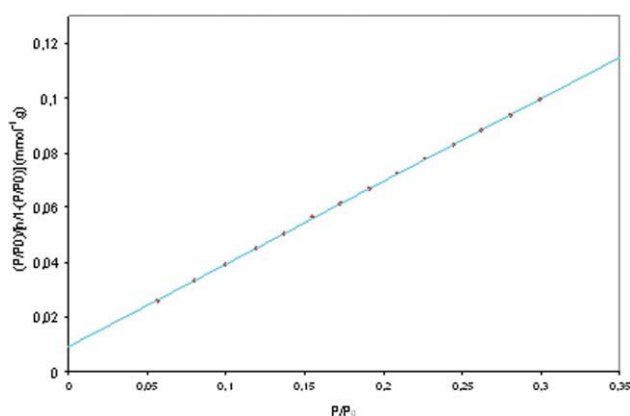


Figure 4 BET line of sample for partial pressures $0.05 < P/P_0 < 0.31$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

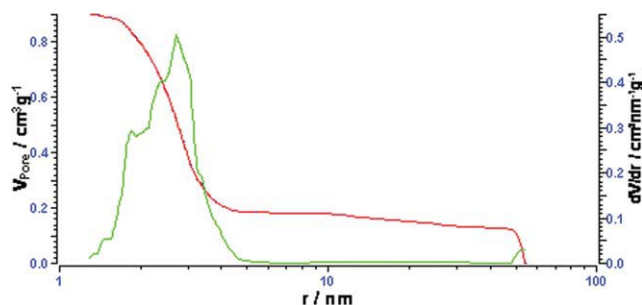


Figure 5 BJH pore size distribution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

normalize the surface coverage, whereas native silica has a monolayer volume of $89.11 \text{ cm}^3 \text{ g}^{-1}$. The BET parameters are all within the range normally observed when the isotherm is adequately described by the BET equation.

Taking into account L_0 and S_{BET} of the modified silica, the average surface density, d , of the attached molecule and the average intermolecular distance, l , can be calculated by applying the following equations:^{45,46}

$$d = N L_0 / S_{\text{BET}}$$

$$1 = (1/d)^{1/2}$$

where N is the Avogadro's number and L_0 is the proportion of functional groups attached on the surface. Results obtained ($d = 0.54 \text{ molecule nm}^{-2}$ and $l = 1.36 \text{ nm}$) confirm an efficiency in the functionalization of the MS. The considerable functionalization degree obtained can be explained as a consequence of its high surface area.

Thermogravimetric analysis

The thermogravimetric curve (Fig. 6) indicates a degradation process between 275 and 780°C which confirms the high thermal stability for the prepared material. The mass loss observed is consistent with the amount of ligand covalently bound to the support (5.65% , 56.5 mg g^{-1} , $280 \text{ } \mu\text{mol g}^{-1}$). All these results provide evidence that the preparation of the functionalized material was successful. Indeed, for the free silica (So), two stages of mass losses are to

TABLE II
Physical Properties of Native Silica and Modified Silica MS

	Specific surface ($\text{m}^2 \text{ g}^{-1}$)	Pore volume ($\text{cm}^3 \text{ g}^{-1}$)	Pore diameter (nm)	Monolayer volume ($\text{cm}^3 \text{ g}^{-1}$)
Native silica	550	0.80	6.000	89.11
Modified silica	314	0.69	2.866	71.96

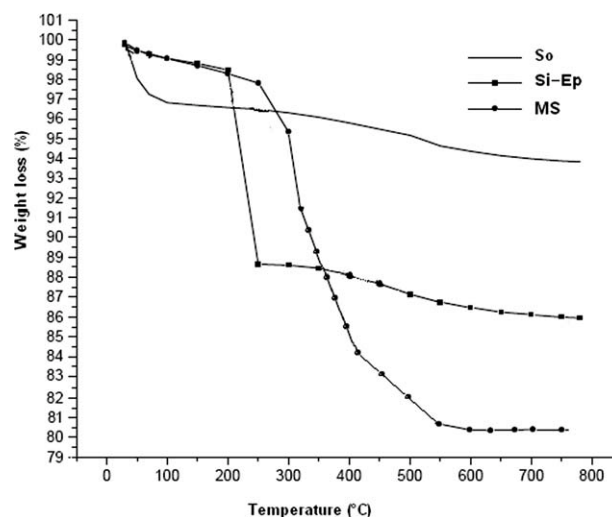


Figure 6 Thermogravimetric curves of free silica (So), epoxy silica (Si-Ep) and modified silica (MS).

be distinguished: the first one corresponds to 3.30% (from 25 to 150°C) assigned with physically adsorbed water; the second stage of mass loss of 2.84% in the 150 – 780°C allotted to the condensation of the free silanol groups which cause siloxane bond formation (Si–O–Si).^{47,48} In addition, the curve involving epoxy groups (Si-Ep) presented a mass loss, after the drainage of physically adsorbed water, of 12.84% in the 150 – 780°C . The final material (MS) showed an increase of mass loss allotted to the decomposition of the organic fraction immobilized on the surface of silica gel, together with the condensation of the remaining silanol groups. The pronounced increase in mass loss for the MS matrix reflects the higher amount of the anchored organic groups.

Chemical stability

Finally, the chemical stability of the newly modified material was examined in various acidic and buffer solutions (pH 1–7). Samples were mixed with different concentrations and stirred at room temperature during 24 h. The change in the degree of functionalization was calculated by elemental analysis of the samples both before and after the chemical treatment. After acid treatment, the percentage of nitrogen in the functionalized silica was not modified ($\%N \approx 1.18$). The high stability exhibited by the attached organofunctional group is presumably due to the length of the pendant group, which binds the C,C-pyridylpyrazole groups to the silica surface. Indeed, it has been shown that when the length of the hydrocarbon bridge was more than two methylene groups, the rupture of Si–C bond did not occur in mineral acid medium, as longer chains do not

have a functional handle which can undergo beta-elimination of the Si cation.^{49,50}

CONCLUSIONS

Modified porous silica with significant porosity ($N_m = 71.96 \text{ cm}^3/\text{g}$), pore volume ($0.69 \text{ cm}^3/\text{g}$), pore size (2.866 nm), BET surface ($314 \text{ m}^2/\text{g}$), and chemical (pH 1–7) and thermal (275–780°C) stability was synthesized. The density of the attached molecules ($d = 0.54 \text{ molecule nm}^{-2}$) and the intermolecular distance ($l = 1.36 \text{ nm}$) were also calculated. Elemental analysis, IR spectroscopy, TGA, and nitrogen adsorption-desorption isotherm were used for its characterization. This new material can be used in various applications quoted in the introduction. Especially, this system can be explored for extracting hazardous metals from water solutions if the high donor properties of nitrogen toward these metals are considered.

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