

S.V.M. DE MORAES¹
 M.T. LARANJO¹
 M. ZAT¹
 T.M.H. COSTA¹
 M.R. GALLAS²
 E.V. BENVENUTTI^{1,✉}

High-pressure effects on nanometric hybrid xerogels, *p*-phenylenediamine/silica and *p*-anisidine/silica

¹ LSS, Instituto de Química, UFRGS, CP 15003, 91501-970, Porto Alegre, RS, Brazil

² LAPMA, Instituto de Física, UFRGS, CP 15051, 91501-970, Porto Alegre, RS, Brazil

Received: 16 March 2004 / Accepted: 31 May 2004

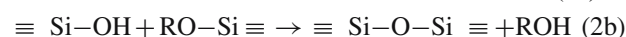
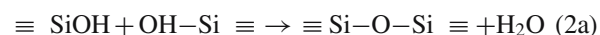
Published online: 29 July 2004 • © Springer-Verlag 2004

ABSTRACT The hybrid xerogels *p*-phenylenediamine/silica and *p*-anisidine/silica were prepared with different surface areas and porosities and they were processed at high pressure (7.7 GPa or ~ 76000 atm) in a quasi-hydrostatic medium at room temperature. The morphologies of the materials were studied before and after the high-pressure treatment by using N₂ adsorption–desorption isotherms, scanning electron microscopy and infrared thermal analysis. The porous hybrid *p*-phenylenediamine/silica presented after the high-pressure treatment a surface-area reduction and an entrapment of organics in closed pores. However, the less porous hybrid *p*-anisidine/silica showed a surprising behavior, a pressure-induced increase in surface area with opening of pores. We propose a mechanism based on the inhibition of the cold sintering process by the organics to explain these results.

PACS 81.20.-n; 81.40.Vw; 81.05.-t

1 Introduction

The sol–gel method is an attractive route to prepare several silica-based materials, with promising properties that allow their potential application as sorbents, sensors, catalysts and optical and electrochemical devices [1–8]. The sol–gel method to prepare silica consists basically in the hydrolysis (Scheme 1) and polycondensation of alkoxy silanes in tetraethylorthosilicate (TEOS) or tetramethylorthosilicate (TMOS) (Schemes 2a and 2b) that result in a cross-linked silica network [9].



Thus, it is possible to insert several organic groups in the silica structure by choosing an appropriate organosilane (R–Si(OR)₃) to be hydrolyzed and polycondensed simultaneously with the TEOS or TMOS. The resulting hybrid materials present a very stable organic phase [10, 11].

The high-pressure technique is an effective tool to be used for compaction of silica-based powder materials, improving

mechanical, optical and morphological properties [12–16]. Costa et al. [17] proposed a cold sintering mechanism to explain the compaction of a pure silica system at room temperature. The high-pressure compaction produces an approach of silanol groups that react to form bridged siloxanes, resulting in a more cross-linked and compacted silica network. In this process the pure silica undergoes a drastic reduction in the surface area, near 100 times, due to the formation of a microstructure with closed pores.

In the present work, the high-pressure technique was used to compact, at room temperature, the hybrid-based silica, *p*-phenylenediamine/silica (*p*-PhAS/silica) and *p*-anisidine/silica (*p*-ANS/silica). The high-pressure effects on silica-containing organics were investigated by using infrared spectroscopy, N₂ adsorption–desorption isotherms and scanning electron microscopy.

2 Experimental

2.1 Synthesis

For the synthesis of the sol–gel organic precursors the *p*-phenylenediamine and *p*-anisidine were activated with sodium hydride in 10 ml of aprotic solvents mixture (toluene:thf) (Merck) (1:1) for 30 min, and 3-chloropropyltrimethoxysilane (CPTMS, Merck) was added. The quantities used were stoichiometric (5 mmol) for *p*-phenylenediamine (Merck), *p*-anisidine, CPTMS and NaH (Acros). The mixtures were stirred under argon at solvent-reflux temperature for a period of 5 h. The solutions were then centrifuged, and the supernatants that contain the *p*-phenylenediaminepropyltrimethoxysilane (*p*-PhAS) or *p*-anisidinepropyltrimethoxysilane (*p*-ANS) were used as sol–gel organic precursors in the two gelation processes. Afterwards, tetraethylorthosilicate (TEOS, Acros) (5 ml), ethyl alcohol (Merck) (5 ml), HF (0.1 ml, Synth) and water in stoichiometric ratio with Si $r = 4/1$ (1.6 ml) were added to the precursor solutions, under stirring. The gelations occur by a fluoride nucleophilic catalytic process, at pH ~ 10 . The mixtures were stored for a week, just covered without sealing, for gelation and solvent evaporation. The resulting xerogels were then extensively washed using the following solvents: toluene, thf, ethyl alcohol, distilled water and ethyl ether. The xerogels were finally dried for 30 min in an oven at 100 °C. The resulting xerogel powders were designated *p*-PhAS/silica and *p*-ANS/silica.

✉ Fax: +55-51/3316-7304, E-mail: edilson@iq.ufrgs.br

2.2 High-pressure technique

For the high-pressure technique, the xerogel powders were initially pre-compacted in a piston–cylinder-type die to approximately 0.1 GPa. The volume of pre-compacted samples was about 0.35 cm³ (diameter of 8 mm and height of 7 mm). The samples were then placed in a Pb container which acted as a quasi-hydrostatic pressure-transmitting medium. The high-pressure processing was accomplished in a toroidal-type chamber at 7.7 ± 0.5 GPa ($\sim 76\,000$ atm) at room temperature [18]. The pressure calibration was accomplished by the fixed-points method [19].

2.3 Infrared analysis

Self-supporting disks of the materials were prepared, with an area of 5 cm², weighing ~ 100 mg. The disks were heated in a temperature range from 100 to 450 °C under vacuum (10^{-2} Torr, 1 Torr = 133.3 Pa), for 1 h. The infrared cell used in this work was described elsewhere [20]. The equipment used was a Shimadzu Fourier-transform infrared (FTIR) spectrometer, model 8300. The spectra were obtained with a resolution of 4 cm⁻¹, with 100 scans.

2.4 N₂ isotherms

The nitrogen adsorption–desorption isotherms of previously degassed solids, at 150 °C, were determined at liquid-nitrogen boiling point in a home-made volumetric apparatus, with a vacuum-line system employing a turbomolecular Edwards vacuum pump. The pressure measurements were made using a capillary Hg barometer. The specific surface areas of the hybrid materials were determined using the BET (Brunauer, Emmett and Teller) [21] multipoint method and the pore-size distribution was obtained using the BJH (Barret, Joyner and Halenda) method [22].

2.5 Scanning electron microscopy

The hybrid xerogel materials were analyzed with a Jeol model JSM 5800 scanning electron microscope (SEM), with 20 kV and 60 000 times magnification.

3 Results and discussion

The synthesis of the sol–gel organic precursors employing a SN₂ reaction between 3-chloropropyltrimethoxysilane (CPTMS) and aromatic amines has been described by using sodium hydride as a base activator [23]. The organic precursors *p*-PhAS and *p*-ANS, synthesized in this work, are illustrated in Fig. 1.

In the presence of tetraethylorthosilicate (TEOS), water and HF catalyst, the organic precursors undergo hydrolysis and polycondensation. The resulting hybrid xerogel materials present a covalent organic–inorganic interface, and the organics can be dispersed in open pores or trapped in closed pores [11].

Infrared thermal analysis is a very effective tool to investigate the presence and the distribution of the organic phase in hybrid xerogel materials with a covalent organic–inorganic interface. The analysis is based on the evolution of the infrared band areas of the organics in relation to the thermal

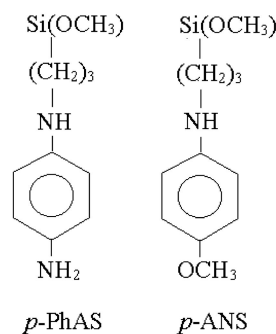


FIGURE 1 Sol–gel organic precursors used

treatment [11]. The band area of the organics dispersed in open pores, when covalently bonded, is almost constant up to 300 °C. However, these organics are completely desorbed when heat treated up to 450 °C, in vacuum. The remaining organic bands that do not vanish are attributed to trapped organics in closed pores [11]. Thus, it is possible to calculate the relative organic coverage, i.e. organic groups that are really on the surface, in open pores. This is obtained by subtracting the band areas corresponding to the organic trapped groups from the band areas of the organic total content. The organic band-area values are obtained by using the overtone silica band at ~ 1870 cm⁻¹ as a reference band. This normalization was necessary, considering the heterogeneity in the disk's thickness, so as to take into account the position changes of the infrared beam.

The infrared spectra of the *p*-PhAS/silica and *p*-ANS/silica materials are presented in Figs. 2 and 3, respectively. The great organic thermal stability observed for the powdered samples heat treated up to 400 °C, in the vacuum cell, is evidence that these groups are strongly bonded to the surface in the covalent form. It is possible to observe that the fraction of organics that remained in the powdered

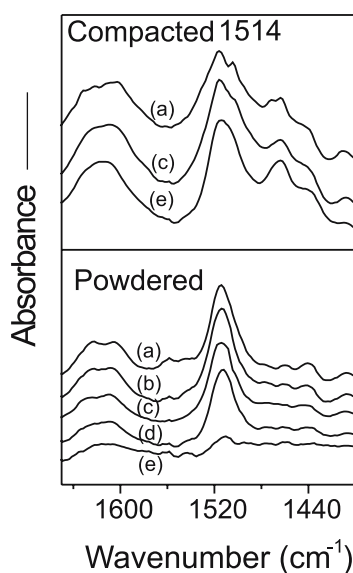


FIGURE 2 Infrared spectra of powdered and compacted (7.7 GPa) *p*-PhAS/silica samples, obtained after heat treatment in vacuum for 1 h up to: (a) 100; (b) 200; (c) 300; (d) 400 and (e) 450 °C. The bar value is 0.5 for both powdered and compacted samples

