Porous Tungstenphosphate Glass Obtained Using a Template-Free Route Based on Controlled Devitrification

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[The vitreous system $6Li_2O$-$18WO_3$-$43CaO$-$33P_2O_5$ (gLWCP) was prepared by a melt-quenching method and separation phase was carried out by a two step heat treatment based in DTA data. The acid leaching of glass-ceramic (gcLWCP) resulted to a porous glass (pgLWCP). The XRD profile of gLWCP showed only a broad peak and ^{31}P MAS-NMR exhibited a broad isotropic signal centered at 12.6 ppm. The Raman spectrum of gLWCP showed a strong band at 940 cm^{-1} due to W-O terminal bonds in WO_6 octahedral, and a shoulder at 880 cm^{-1} due to stretching vibrations of P-O terminally bonded PO_4 tetrahedral linked to WO_6 octahedra. For gcLWCP, the XRD pattern showed broad peak related to non-crystalline phase and peaks related to a crystalline phase β-$Ca_2P_2O_7$ phase – CP phase. The occurrence of this phase is also confirmed by ^{31}P MAS-NMR (two sharp peaks around 7.5 ppm related to Q^1 units) and Raman spectroscopies. The XRD pattern of pgLWCP also exhibit only a broad peak as observed in the gLWCP. The backscattered SEM image of gcLWCP revealed the presence of two phases, *i.e,* the CP phase embedded in a vitreous W-rich phase].

INTRODUCTION

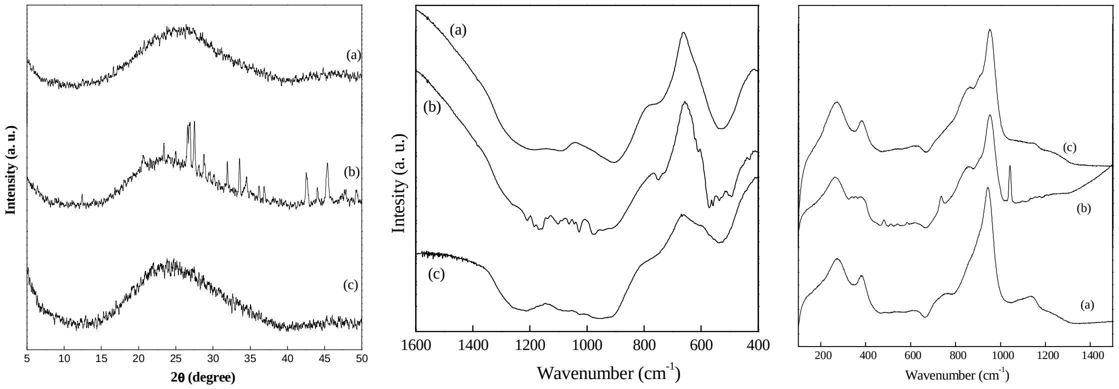
Porous materials are extremely important in the fields of nanotechnology, integrated chemical systems, and cooperative interactions in reactions performed in confined environment. There is an increasing interest in designing and developing porous materials with stable porous texture for high-temperature separation and catalytic application[i,ii]. It has been demonstrated that every properties of nanophase materials are interesting for various technological applications because of the specifically size related properties of crystalline domains or crystallites. In integrated chemical systems (ICS), the pore size of a support material determines the maximum size of the particle synthesized within it. The pores that typify these structures can be considered as 'micro-chambers', which fulfill, at the same time, a template role. The size, the morphology and the reactivity of the particle will depend on the dimensions, morphology, texture and chemical nature of the surface of pores. The focus of this work was the fabrication and characterization of a functional porous support using template-free route by controlled devitrification following leaching from tungstenphosphate glass as precursor.

EXPERIMENTAL

Original glass samples of nominal composition $6Li_2O$-$18WO_3$-$43CaO$-$33P_2O_5$ (mol %), gLWCP, were prepared by melt-quenching method (melting: 1200ºC/1h; anneling: Tg+40°C/2h). Glass-ceramic samples (gcLWCP) were prepared by a thermal treatment of the glass plates at 515 ºC for 20 h (nucleation step) and subsequently at 680 ºC for 12 h. The resulting glass-ceramics (gcLWCP) were immersed in 1.0 mol L^{-1} HCl aqueous solution and kept for 24 h at room temperature, in order to obtain porous glass (pgLWCP). The nature of the phases of the glass-ceramics before and after acid leaching was characterized by XRD, IR, Raman, ^{31}P MAS-NMR and SEM.

RESULTS AND DISCUSSION

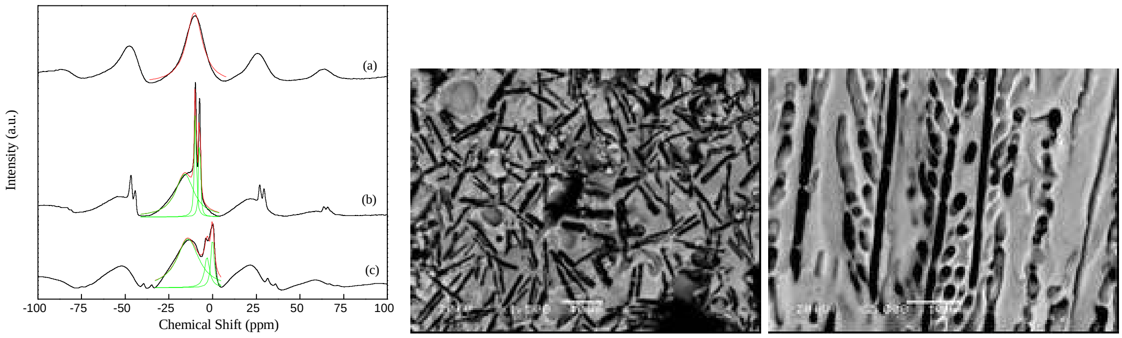
The gLWCP showed XRD pattern typical for non-crystalline solid, presenting a broad peak near $2\theta = 25.7°$ (Fig.1a). The Raman spectrum of gLWCP exhibited a broad band centered at 940 cm^{-1} assigned of the W-O bonds in WO_6 group and shoulder at 880 cm^{-1} assigned to P-O-W bonds (Fig. 2a). The symmetric stretching of these bonds appear at 910 cm^{-1} in IR spectrum (Fig. 3a). In spite of the very close interplanar distances between the several calcium phosphate phases, the XRD pattern of gcLWCP (Fig. 1b) suggested the presence of the crystalline β-$Ca_2P_2O_7$ phase associated with a non-crystalline phase due the presence of the broad peak. The IR spectrum of the gcLWCP (Fig.3b) confirmed the presence of pyrophosphate groups, characterized by the band at 727 cm^{-1}, characteristic of the β-$Ca_2P_2O_7$ ν(P-O-P)sym mode. The occurrence of this group is also confirmed by Raman spectroscopy (Fig.2b), with bands at 737 cm^{-1} [$\nu(PO_3)$sym] and 1047 cm^{-1} [ν(P-O-P)sym]. The IR and Raman spectra of gcLWCP keeping the characteristics bands of vitreous phase. The ^{31}P NMR-MAS spectrum of gLWCP show broad isotropic signal centered at -10.0 ppm consistent of the typical structural disorder of vitreous materials (Fig.4a). The value of the chemical shift is consistent with the predominance of Q^1 units belonging to pyrophosphate chains. The ^{31}P NMR-MAS spectrum of gcLWCP (Fig. 4b) shows two sharp signals centered at -9.8 and -7.4 ppm attributed the presence of the crystalline β-$Ca_2P_2O_7$ phase[iii] and a broad signal centered at -15.9 ppm. This result confirms that the devitrification leads the formation of the β-$Ca_2P_2O_7$ and vitreous W-rich phase, in agreement with IR and Raman data. The gLWCP presents a single devitrification peak at 680 °C (crystallization activation energy equal to 425 kJ mol^{-1}) and data suggested the separation phase of β-$Ca_2P_2O_7$ without disrupting of the P-O-W bonds.



(1) (2) (3)

Figure - (1) Powder XRD patterns, (2) IR spectra and (3) Raman spectra of (a) gLWCP, (b) gcLWCP and (c) pgLWCP.

For pgLWCP, the IR (Fig.2c) and Raman (Fig.3c) bands associated to P-O-P groups are not observed, indicating that the β-$Ca_2P_2O_7$ phase was leached by the acid. The XRD pattern of gpLWCP exhibited the same profile of the gLWCP indicating the preparation of the porous glass with tungstenphosphate network. In Raman spectrum of pgLWCP the band at 880 cm^{-1} is more intense than gLWCP. This result evidences an increase in the polymerization degree between PO_4 and WO_6 units aiming to reduce the number of non-bridging oxygens in consequence of the decrease in concentration of Ca^{2+}, that acts as modifier network. This hypothesis is confirmed by increase of the intensity in IR spectrum of the band at 970 cm^{-1} assigned at υ_{as}(P-O-W) and by decrease of the band at 520 cm^{-1} attributed the disrupt of the P-O-W bonds due the increase of the Ca^{2+} concentration. Additionally, it appears the band at 630 cm^{-1} assigned to υ_{s}(P-O-W). The increase of the network polymerization degree associated with the increase of W/P and W/Ca ratios promotes the increase glass stability in tungstenphosphate glasses[iv]. The ^{31}P NMR-MAS spectrum of pgLWCP (Fig. 4c) exhibited a broad signal centered at -14.2 ppm indicating the increase of polymerization degree and two signals at -3.1 and 0.1 ppm associated the residual presence of the β-$Ca_2P_2O_7$ phase. XRF data confirmed the presence of the W, Ca and P in the pgLWCP.



(4) **(5)** **(6)**

Figure - **(4)** ^{31}P MAS-NMR spectra of (a) gLWCP, (b) gcLWCP and (c) pgLWCP; Backscattering SEM micrograph of the fracture of **(5)** gcLWCP and **(6)** pgLWCP.

The backscattered SEM image of gcLWCP reveals the presence of two phases, *i.e*, the β-$Ca_2P_2O_7$ phase embedded in a vitreous W-rich phase (Fig. 5). SEM microscopy confirmed the preparation of the porous glass with skeleton of tungstenphosphate with three-dimensional network structure.

CONCLUSION

In summary, the data reported here allows us to conclude that fabrication of original porous glass monoliths with skeleton of non-crystalline tungstenphosphate employed the template-free route based on the controlled devitrification of the glass precursor following the leaching. Further studies are being carried out in our laboratory aimed at the compositional determination of the porous glass and the use this functional porous material as host for integrated chemical systems.

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