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Solids

Adherence of molecules to silica glass surface: Experimental results and theoretical calculations

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Abstract

The adherence of molecules to surfaces is used in a wide scope of technological applications. In this work we study the attachment of molecules onto porous silica glass surface obtained from a Vycor glass, after glass-glass phase separation and leaching of the soluble phase with water. Nitrogen adsorption at 77 K was used for the determination of the specific surface area (BET area) and pore size distribution on the leached glass. The adherence onto the glass surface, of model molecules methylene blue (MB) and eosine yellow (EY), with positive and negative electrical charges respectively, was studied. The adsorption kinetics was determined from aqueous solutions using UV-VIS spectroscopy. It was found that the silica glass surface as prepared in this work is selective for positively charged molecules at pH≈5.20, an adsorption of 1 mg MB per gram of glass was found for methylene blue, and almost null adsorption for eosine yellow. First principles calculations were performed using the Density Functional Theory in order to model the interaction between both molecules and the glass surface.

Keywords: porous silica; adsorption; methylene blue; eosine yellow

1. Introduction

Porous silica glasses are high specific area materials which due to its high chemical corrosion resistance have been considered among other applications for nuclear wastes immobilization [Aparicio et al., 2006]. In this work we study the properties of this material for attaching molecules with different electrostatic charges when dissociated in an aqueous solution. It is a complex problem where the glass surface chemistry depends on the pathway used for obtaining the porous glass and on the solution pH [Parffit G. D., 1976], and the adherence will also depend on different chemical species that are in solution. The latter aspect could be determining if for example we are interested in separating one chemical species from others using their adherence kinetics on silica surface.

In order to understand the adherence mechanisms from our experimental observations, first principles calculations were done using the Density Functional Theory. This tool is essential to tailor surface selectivity.

2. Experimental Methods

2.1 Production of vitreous silica

A borosilicate Vycor type glass with composition 65.6 SiO_2-27.8B_2O_3-6.0Na_2O-0.6 Al_2O_3 wt% was chosen for the production of vitreous porous silica [Aparicio et al, 2002]. The precursor powders, SiO_2 Fluka Analytical 99.87% purity- $B_4Na_2O_7.10H_2O$ Sigma Aldrich 99.5 % purity, B_2O_3 Riedel – De Haë purity 99.94% and Al_2O_3 Sigma Aldrich 99.7 % purity were dried at 90 °C for 2 hours, except $B_4Na_2O_7.10H_2O$. Subsequently, each reagent was weighed on an analytical balance, in adequate amounts to obtain 100 g of glass. The mixture of powders was homogenized by mechanical mixing during 2 hours. Then, it was placed in a platinum crucible and heated up to1600 °C at a heating rate of 10 °C/min, left for homogenization 2 hours and splat cooled to obtain glass slices of about 3 mm thick avoiding glass-glass phase separation. Hereafter, the glass produced is referred to as BSN.

The pieces of glass were heated at a temperature of 660 °C for glass-glass phase separation during 12, 24, 36, 48, 72 and 144 hours. After heat treatment, the glassy material was cut into small pieces with rectangular parallelepiped form of approximate dimensions 5x3x4mm³. We assumed here that the borosilicate glass phase-separates into an rich insoluble silica phase and a water soluble Na_2O-B_2O_3 phase. Leaching experiments were conducted by immersion in distilled water at 90 °C and characterized by measuring the mass percent removed as a function of time, using initial masses ranging between 50 and 60 mg. Treatment times were taken between 4 and 32 hours, and every process was done in triplicate.

2.2 Characterization

Characterization of the glasses included, chemical, morphological, structural, microstructural and textural studies.

2.2.1 Qualitative analysis of the optical characteristics of glass

It was checked that the glass prepared by splat-cooling was free from visual defects and that after glass-glass phase separation the whitish colored appearance was homogeneous all through the sample. Inhomogeneous parts were separated.

2.2.2 X-ray diffraction

In this study, structural analyzes were performed with X-ray diffraction on powders of vitreous samples from glasses separated in two glassy phases at 660 °C, at times ranging between 12 to 144 hours as well as non-heat treated sample. We used a Philips PW1700 diffractometer belonging to the Materials Characterization Department, using CuKα radiation (λ=1.54054Å) in a scanning range between 10° and 70° (2θ) at a rate of $0.025°s^{-1}$.

2.2.3 Infrared Fourier transform spectroscopy

The glasses were analyzed using infrared Fourier transform spectroscopy (FTIR) to determine qualitatively the functional groups present in the samples. We used a Perkin Elmer 400 with Spectrum highly sensitive detector of Mercury-Cadmium-Telluride (MCT), belonging to the Department of Physical Chemistry. Analyses were made in a sweep between 4000 and 450 cm^{-1} at a resolution of 4 cm^{-1} and taking 30 scans for each sample. The spectra were corrected by subtracting the background spectrum and normalized. For the preparation of the samples a few milligrams of powdered glass were taken, and mixed in an alumina mortar with ~ 35 mg of potassium bromide (KBr, Fischer, 99.9%), the mixture was then uniaxially pressed at 250 kg/cm^2 forming a translucent specimen.

2.2.4 Scanning electron microscopy

During the course of this investigation, glasses were analyzed using scanning electron microscope FEG Philips NovaNano 230 and 515, both from the Department of Materials Characterization.

Observations were made using this technique on samples of vitreous material after being leached, from both the surface and inside. Thus, preparation of samples for surface analysis was based only on placing the glass on the sample holder of the equipment and as such material is not a good conductor of electricity, it was deposited over it a layer of approximately 1000 Å of gold before observation. On the other hand, to analyze the internal morphology of the samples, these were included in an epoxy resin and subsequently polished with abrasive paper No. 320, 400, 600/1200 and 2400, then with diamond pastes 6, 3 and 1 micron and ¼ micron alumina. The inclusions were washed with industrial grade ethyl alcohol and dried in air. Before their characterization they were also coated with a layer of gold.

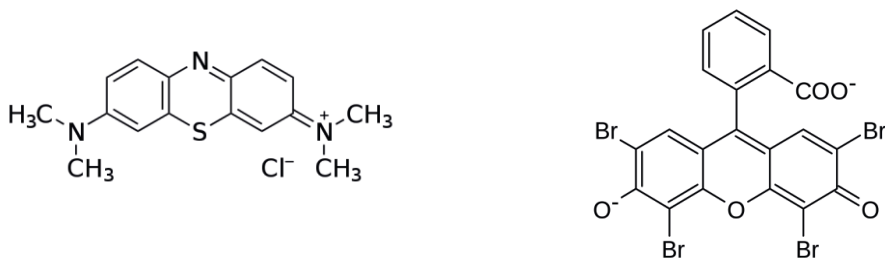### 2.2.5 Adsorption/desorption of methylene blue and eosine yellow

Figure 1 (left). Molecular structure of dissociated methylene blue.   **Figure 2** (right)**.** Molecular structure of dissociated eosine yellow.

Methylene blue, which molecular structure is shown in Fig. 1, adsorption kinetics on porous matrices obtained after different thermal treatments at 660 ºC during 12, 72 and 144 hours were done. The kinetics was characterized measuring the absorption of visible light at 661nm wavelength, where methylene blue presents an absorption peak with a spectrophotometer UV/Vis double beam Perkin Elmer model Lambda 35.

Also, eosine yellow (see Fig. 2) adsorption kinetics was studied, using the same procedure at a wavelength of 518 nm.

3. Results and discussion

3.1 Leaching of soluble phase and scanning electron microscopy

Regardless of its thermal history, the mass loss behavior was similar, although not its microstructure (See Fig. 3). The sample treated at 660 °C for 12 hours reached a removal percentage of 28.9±0.8% of its initial mass when was left in distilled water at 90 °C for 32 hours, while glasses with longer treatment, 72 and 144 hours, managed to lose a 26.9 ±0.7% and 27.3±0.9 % respectively after the same leaching conditions.

After 32 hours of leaching, it is reached a state of saturation in the elimination of the soluble phase. Now, given that the nominal initial composition of the glass is 65.6SiO2-27.8B2O3-6.0Na2O-0.6Al2O3 (wt%) and the soluble phase which is rich inB2O3-Na2O, the maximum mass loss could be 33.8%. The difference between measured and expected value can be explained in part by sodium borohydride volatilization in the glass melting process and secondly by a partially solubilization of B_2O_3 in the silicate glass.

Finally, as to establish a standard time and leaching process, it was decided hereinafter heat treating at 660 °C for 12 hours, leaching in distilled water at 90 °C for 24 hours and after removing the fluid post-treatment, add again50 ml of distilled water and maintain at the same temperature for two hours and then left to dry the samples at least 24 hours.
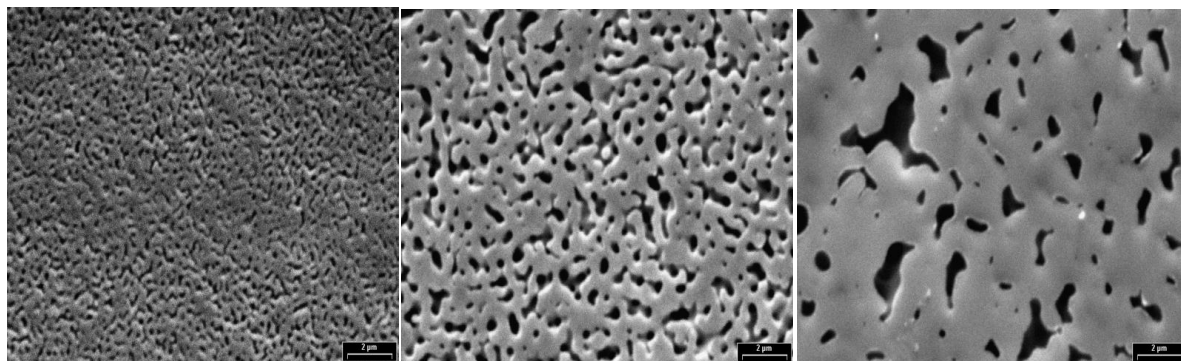

Figure 3. Scanning electron microscopy micrographs of of the glass cubes surface treated at 660 ° C for A) 12, B) 24, C) 36, D) 48, e) 72 and F) 144 hours and subsequently leached in distilled H_2O at 90 ° C for 24 hours. The scale bar length is 2um.

Nanoporosity was found both on the blocks faces and in the cube inside. Nitrogen adsorption-desorption isotherms showed that porosity is mainly in the size range 20A-150 A for heat treatments at 660C during 24 and 78 hs, although glass heat treated during 12 hs showed a narrower pore size range : 50A-150A.

3.2 X-ray diffraction

X-ray diffraction of the glass BSN1 without heat treatment, shows two halos which correspond to an amorphous structure (Fig. 4), within the limit of detection of the technique which is about 1% in volume. Likewise, in the phases separated samples, the X-ray diffractograms showed a similar behavior without diffraction peaks. Accordingly, one may think that the mechanism of phase separation occurs in the material due to the immiscibility of phases for the decomposition.
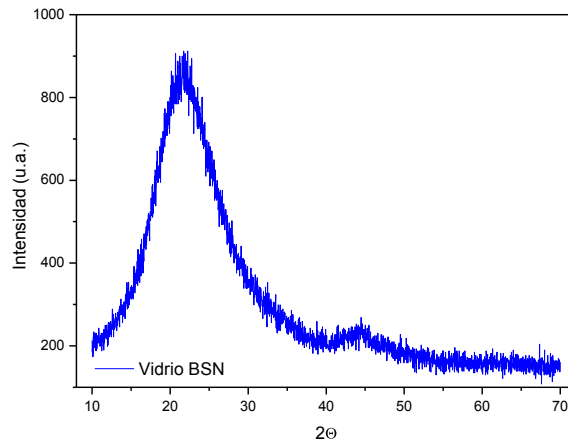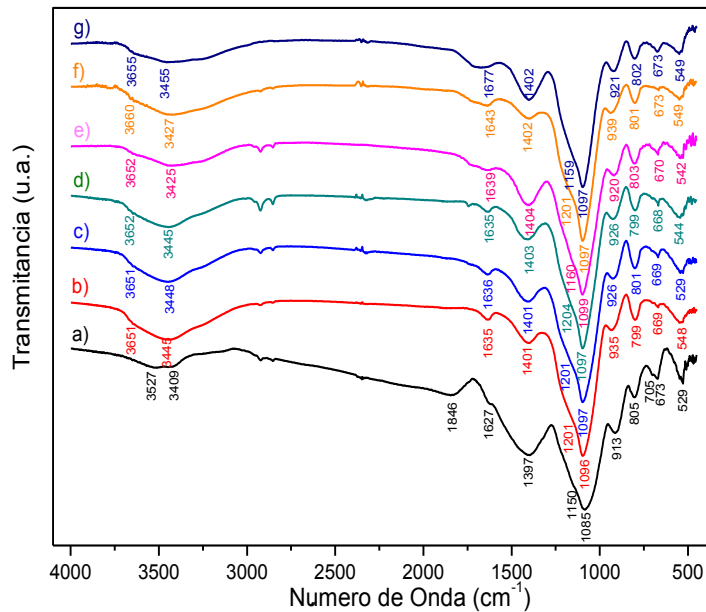

Figure 4. X-ray diffractogram of BSN glass.

Figure 5. FTIR Spectra of: a) Phase separated BSN glass, and samples b) S12L, c) S24L, d) S36L, e) S48L, f) S72L y g) S144L.
(S=phase separated, 12=12 hours at 660C, L=lixiviated in distilled water)

3.3   Infrared Fourier transform spectroscopy

Spectra of the glass heat treated at 660 °C between for different times from 0 to 144 hs, are shown in Figure 5.

In this spectra is evident the band in the region of 3500-3380 cm^{-1} which can be attributed to the extension of Si-OH groups and stretching vibrational mode of the O-H bond of residual molecular water, whose presence is confirmed by the band between 1650-1630 cm^{-1} corresponding to the flexing of the links H-O-H. The band near 1400 cm^{-1} corresponding to the asymmetrical vibration of extension of the link B-O in BO$_3$ units. Towards lower wave number is a strip of high relative intensity around 1090 cm^{-1} with a shoulder near 1145 cm^{-1} which are assigned to the stretching vibrations of the Si-O-Si in the components longitudinal optical (LO) and transverse (TO) in the SiO$_4$ tetrahedron, respectively. The band at 1145 cm^{-1} can also be attributed to the vibration of B-O bond in the presence of sodium borate.

The vibration located in the range of 925 and 910 cm^{-1} is associated with B-O bond in BO$_4$ units and the region between 680 and 670 cm^{-1} may be due to vibration B-O boroxol rings. In these bands is evident the effect of heat treatment in the spectra is observed a shift to lower wave numbers relative to the untreated sample and which may be due to the formation of Si-O-B, by the incorporation of units BO4 SiO$_4$ tetrahedral units. It also shows the presence of a shoulder on the 700 cm^{-1} corresponding to the bending vibrations of links B-O-B. The band of low relative intensity at 800 cm^{-1} may be associated with the stretching vibrational mode of broken Si-O bridges. The existence of the band between 550 and 530 cm^{-1} can be attributed to two events in the first bending vibration of Si-O-Si and phase separation in glass, where involved tensile and bending vibrations of SiO$_4$ group and B-O.

The band around 3650 cm-1 attributable to the free silanol group, SiO-H, which may come from hydrolytic dissolution of bridging oxygens, on the material surface, as shown in reaction 2.1, or as this glass containing small amounts of sodium ions in its structure, which may follow an attack mechanism as described Equation 2.2, resulting in both cases the appearance of silanol functional group.

$$\equiv\text{Si-O-Si}\equiv + \text{H}^+ + \text{OH}^- \rightarrow \equiv\text{Si-OH} + \text{HO-Si}\equiv \qquad (2.1)$$
$$\equiv\text{Si-O-Na}^+ + \text{H}^+ + \text{OH}^- \rightarrow \equiv\text{Si-OH} + \text{NaOH} \qquad (2.2)$$

On the other hand, there is a significant decrease in the relative intensities of the bands related to vibrations of B-O bonds, 1400 and 670 cm-1 result from the removal by leaching of the soluble phase rich in boron and sodium. This statement is argued in the fact that the intensity associated with a vibration IR is directly related to the functional group concentration in the sample.

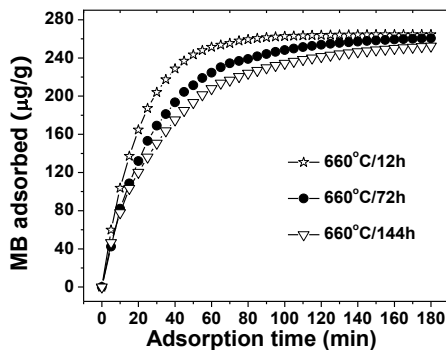*3.4 Methylene blue and eosine yellow adsorption*

Fig.6 MB mass absorbed as a function of time for different porous SiO2 samples from a 4 mg/l aqueous solution.
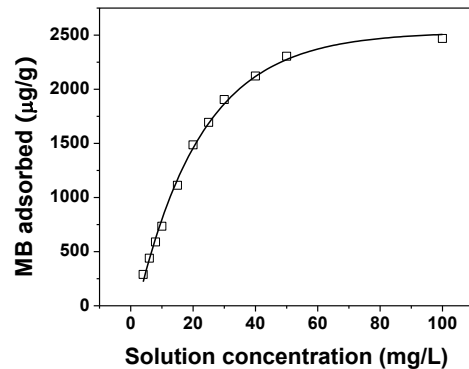
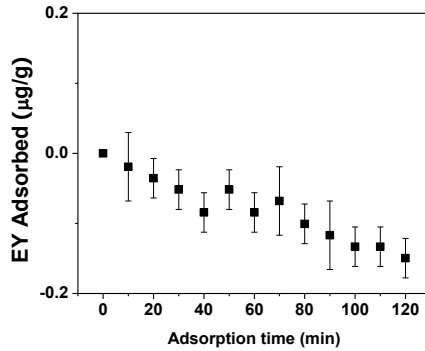Fig.7 Saturation adsorption as a function of solution concentration. The error in each measurement is ±20µg/g.

Fig.8: Eosine yellow mass absorbed as a function of time from a 4 mg/l aqueous solution. The negative slope is due to experimental drift of the measurement device.

MB desorption fraction, at room temperature, reached a value of 70% in alkaline elements 1M solutions, 50% in divalent terreous-alkaline Ca++ and less than 10% in distilled water. The larger the alkaline element concentration the faster de desorption kinetics.

4. Theoretical calculations

First principle using Density Functional Theory (DFT) calculations were performed in order to obtain insights into the energetics involved in the adhesion/repulsion of the Eosine and the Methyle blue molecules on the glass surface.

The simulation of glass surface at the quantum mechanical levels is a challenging task. The main bottleneck is the big size of the supercell and the computational resources needed. An accepted approximation for understanding the local interaction of molecules and glass surfaces is to replace the surface by a crystal surfaces.

The cristobalite structure of SiO_2 is known to be the crystal polymorph that mostly reproduce the physical characteristics of glass thus a crystal surface cut from it is usually used in order to reproduce a surface local environment similar to the one seen by a molecule close to the amorphous phase surface.

Different representative orientations of the molecules positioned close to the 001 surface of the crystoballite were the starting points of the DFT calculations.

The adhesion energy of a molecule to the glass surface is usually defined $E_{ad}=-(E_{tot}-E_{molecule}-E_{surface})$

Where E_{tot} is the total energy of the fully relaxed system of the molecule plus the surface, $E_{molecule}$ and $E_{surface}$ represent the energy of the lone molecule, and relaxed surface respectively. Defined in this way, E_{ad} would quantify the energy needed to remove away the molecule from the equilibrium position at the proximity of the surface to a position far away from it.

We obtained for the system MB molecule-glass surface $E_{ad}=+3.7$ eV , while for dissociated EY $E_{ad}=-2.6$ eV. These results predict an attractive interaction between the $SiO2$ surface and the MB molecules while a repulsive interaction is expected between the $SiO2$ surface and the EY molecules, which agrees with the experimental results. More details about these calculations are shown in Nuñez et al.,2013.

5. Conclusions

We optimized a process to prepare SiO2 porous glass with sub micrometric porosity by leaching with water the soluble glass phase of a glass-glass phase separated sodium borosilicate glass. Using FTIR found the absorption bands associated with B-O bonds of the soluble phase and determined the best leaching procedure to minimize the soluble phase content.

Nanoporosity was found both on the blocks faces and in the cube inside. Nitrogen adsoption-dessorption isotherms showed that porosity is in the size range 20A-150 A for heat treatments at 660C during 24 and 78 hs, although glass heat treated during 12 hs showed a narrower pore size range : 50A-150A.

Through UV-VIS spectroscopy, when immersed in an aqueous solution of 1mg/l Methylene Blue (MB), it was determined that after a few hours the sponge saturated at an adsorption of 250 μg/g. Smaller pores (larger specific porosity) showed a slightly faster adsorption kinetics.

Saturation adsorption showed a linear relationship with MB concentration, at least in the range of studied MB concentrations: 1-16 mg/l .

MB desorption fraction, at room temperature, reached a value of 70% in alkaline elements 1M solutions, 50% in divalent terreous-alkaline Ca++ and less than 10% in distilled water. The larger the alkaline element concentration the faster de desorption kinetics.

The striking results found for the adsorption of MB by this SiO2 glass, contrasts with the null adsorption found for eosineyellow (EY). Since MB molecule has an effective positive charge and EY has negative charge, we conclude that electrostatic forces are responsible for the MB attachment to the SiO_2 surface.

References

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