Experimental report

16/02/2017

Proposal: **6-02-559** **Council:** 10/2014

Title: Molecular Interaction of volatile organic compounds (VOCs) inside Silica and hybrid silica xerogels

Research area: Materials

This proposal is a new proposal

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Samples:
phenyltriethoxysilane: C6H5Si(OC2H5)3
tetraethoxysilane: Si(OC2H5)4
methytriethoxysilane: CH3Si(OCH3)3
ethyltriethoxysilane: C2H5Si(OC2H5)3

Instrument	Requested days	Allocated days	From	To
IN1 LAG	5	7	24/04/2015 03/10/2016	27/04/2015 07/10/2016

Abstract:

Silica and hybrid silica xerogels with synthesis of vapochromic complexes are used as fiber-optic sensors (FOS) to analyze volatile organic compounds (VOCs). Most of the FOS are based on a ligth intensity change produced by the analyte. The response corresponds to a global change of the absortion spectra and it is explained as a variation in the refraction index that modifies the reflected optical signal in a wawguide i.e. This requires optimizing the sensor geometry and the physico-chemical properties of the xerogel film, with materials designed specifically for each analyte. Silica and hybrid-silica xerogels allows to analyze vapors.

The aim of this proposal is to measure the vibrational spectra on Lagrange of different hybrid xerogels using different silica precursors in order to obtain information of the:

1) Structure of the ordered domains promoted by the incorporation of the ethyl groups.
2) Molecular interaction of volatile organic compounds (VOCs) inside Silica and hybrid silica xerogels.

These results will be compared with ab-initio molecular dynamics simulations that will provide time-averaged molecular conformations of the different structures of the ordered domains.

Molecular Interaction of volatile organic compounds (VOCs) inside Silica and hybrid silica xerogels

Silica xerogels have been used as sensing elements in fiber optic sensors to analyze vapors of water, acetone, butanamine, cyclohexane, dichloromethane, chloroform, or toluene[1,2]. Silanol groups on the surface of the xerogel act as weak acids and may interact with molecules that contain lone pairs of electrons, such as acetone; π-electrons, such as toluene; or hydroxyl groups, such as alcohols. The surface chemistry and the porous texture determine the response. Silica xerogels are hydrophilic materials, consequently, water interferes when measuring the response of volatile organic compounds in room conditions. Hybrid-silica xerogels offer several advantages over silica xerogels to develop more sensitive and selective sensing elements because both surface chemistry and porous texture can be tuned.

Incorporation of alkyl or aryl functional groups into the xerogels promote the formation of ordered domains dispersed in an amorphous matrix, as XRD-diffractograms and TEM micrographs confirmed. On the other side, FTIR on hybrid-silica xerogels revealed the shift of the band around 1092 cm^{-1}, found in silica xerogels and characteristic of siloxane bonds, to lower wavenumbers; and the presence of a new band at around 1128 cm^{-1} that has been attributed to cube-like T^8-structures. Thus, IR spectra reflect the structural modifications when alkyl or aryl groups are incorporated into the structure of xerogels, which are related to the substitution of the oxide ions that bridge silicon ions and silanol groups by non-bridging organic groups Besides, the alkyl groups appeared to stabilize the fourfold siloxane ring in the xerogels. However, mass spectroscopy results indicated fragments with polymeric distribution as well. Therefore, the structure or the ordered domains are still an open question and the experimental results obtained at the Laue-Langevin Institute can help to clarify some structural characteristics.

In order to get deep inside the structure, measures were performed using mainly the Cu220 monochromator to obtain the bands related to structural siloxane bonds, as well as the signals related to the presence of organic groups, $(Si\text{-}O)_4$ rings vibrations and the open cage structure. The DOS have been measured at 10 K and at 77 K (The Debye Waller factor sems to be low to correctly increasing temperature).

Results

Several spectra were obtained from hybrid xerogels synthesized from different silica precursors: tetraethoxysilane (TEOS), methytriethoxysilane (MTEOS), ethyltriethoxysilane (ETEOS) and phenyltriethoxysilane (PhTEOS). As an example, Figure 1 shows the spectra of hybrid xerogels prepared from mixtures of TEOS and MTEOS. The presence of the band related to water at ~550 cm^{-1} is the main feature of the xerogel synthesized from TEOS. The intensity of this band decreased with increasing the percentage of MTEOS, which also resulted in new bands at approximately 772, 1275 and 1411 cm^{-1}. Increasing MTEOS content caused structural changes in the skeletal SiO_2 network, which is in agreement with the behavior observed for these species in previous works[3,4].

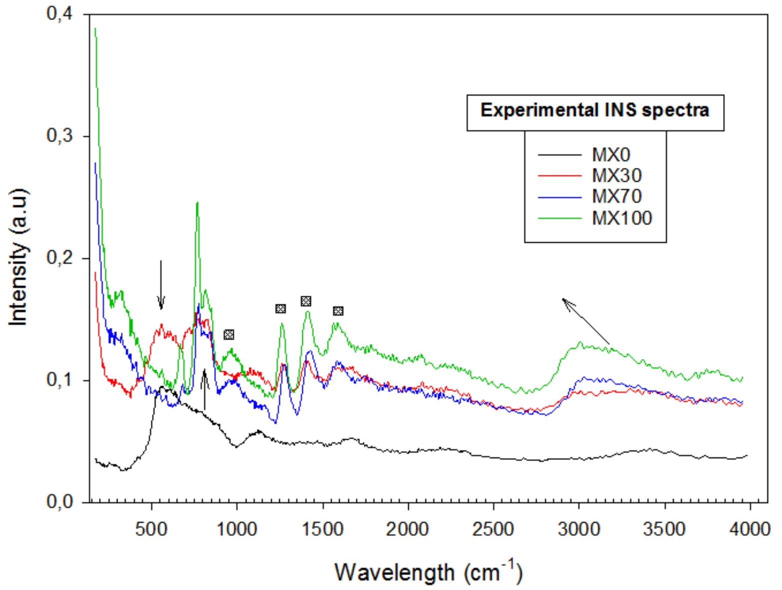

Figure 1: INS spectra obtained on a silica hybrid xerogel (TEOS/MTEOS) for different molar percentages of MTEOS: 0% (MX00), 30% (MX30), 70% (MX70) and 100% (MX100).

Besides, molecular interaction of xerogels with water vapor and volatile organic compounds (methanol, ethanol and cyclohexane) .The samples have been prepared ex-situ. Figure 2 shows the spectra of the spectrum for the xerogel obtained from TEOS before (blue) and after degassing the sample (black). The vibrational bands corresponding to the adsorbed water on the xerogel are identificable at around 550 cm^{-1}. These results reveal that the presence of hydroxyl groups on the surface of TEOS xerogel contribute to the hydrophilic character of silica xerogels. Also, this result is the starting point for future new proposals to study the mechanism of water adsorption on silica hybrid xerogels, the influence of water on the silica network and the hydro-phobic/philic character of the xerogel depending on the different amount of the precursors used in the synthesis (TEOS:RTEOS).

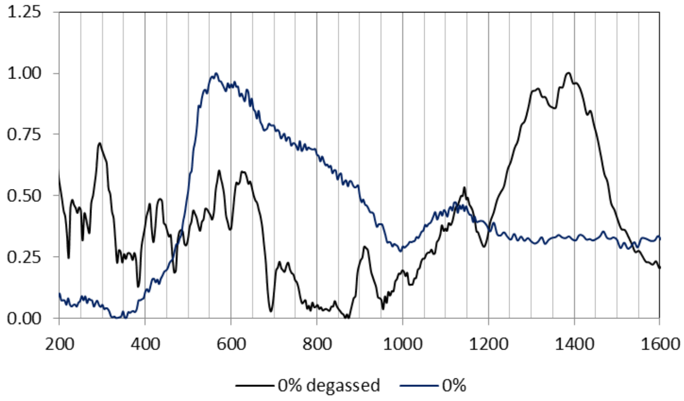

Figure 2: INS corresponding to a TEOS xerogel, MX00, (Blue) and the same xerogel after degasification (black).

In parallel, ab-initio molecular dynamics simulations performed in collaboration with the C-Lab at ILL have provided the theoretical Vibrational Density of States (VDOS) that can be directly compared with the experimental results. We performed a theoretical cage model of hybrid xerogels synthesized from mixtures of MTEOS and TEOS at DFT level using Gaussian03. In these models, the final structure has been used to calculate the vibrational spectrum with the module DMol3 of Materials Studio. This output was used to calculate the INS spectra with the LAMP program. After that, it was compared with the experimental spectrum.

We are currently analyzing and discussing these results to write a manuscript that will be sent to a scientific journal.

References

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(2) Echeverria, J. C.; de Vicente, P.; Estella, J.; Garrido, J. J. *Talanta* **2012**, 99, 433-440.

(3) Rios, X.; Moriones, P.; Echeverría, J. C.; Luquin, A.; Laguna, M.; Garrido, J. J. *Adsorption* **2011**, *17*, 583-593.

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