Structural unit determination in silica nanoparticles using infrared micro-reflectance spectroscopy

Mireia Sainz-Menchón[1], Iñigo González De Arrieta*[2], Abdelali Zaki[2], Franck Fayon[2], and Gabriel López[1]

[1]Zientzia eta Teknologia Fakultatea [Euskal Herriko Unibertsitatea] – Spain
[2]Conditions Extrêmes et Matériaux : Haute Température et Irradiation – Université d'Orléans, Institut de Chimie du CNRS, Centre National de la Recherche Scientifique – France

Abstract

Characterization of the structural units of glasses is an essential part of amorphous materials research, with implications for all kinds of properties, from chemical reactivity to crystallization. The relative proportions of units in silicate glasses can be quantified by magic-angle spinning 29Si nuclear magnetic resonance (MAS-NMR) spectroscopy. Simpler alternatives include Raman spectroscopy, which is affected by luminescence, and infrared spectroscopy, which requires the use of deconvolution techniques to resolve structural information from the broad absorption bands. Furthermore, if the materials under study are nano-sized, extracting quantitative information about their structure from infrared spectroscopy is even more complicated, as the effect of porosity needs to be taken into account through so-called effective medium theories.
In this work, silica nanoparticles produced from the hydrolysis of tetraethyl orthosilicate have been investigated using infrared micro-reflectance spectroscopy and nuclear magnetic resonance spectroscopy. Colloidal silica was chosen because of its chemical and structural simplicity, with only H atoms acting as modifiers of the glass network. The use of micro-reflectance, instead of transmittance or attenuated total reflectance, allows for greater accuracy and reproducibility between samples. The results are analyzed through the Landau-Lifshitz-Looyenga effective medium approximation (1) and a robust deconvolution procedure for the absorption bands, in which each component is attributed to a microscopic origin (2). Excellent agreement is found between infrared and NMR spectroscopies, lending credence to this technique as a simple and accurate, albeit less precise, alternative for structural unit quantification. Because of the generality of this technique, it could be easily extended to other silicate nanomaterials (3).

References

(1) I. González de Arrieta, L. del Campo, D. De Sousa Meneses, "Infrared spectroscopy of CeO2 nanoparticles using Bergman's spectral representation: effects of phonon confinement and lattice strain", *Physical Chemistry Chemical Physics* **23**, 13095 (2021).

(2) D. De Sousa Meneses, M. Eckes, L. del Campo, C. N. Santos, Y. Vaills, P. Echegut, "Investigation of medium range order in silicate glasses by infrared spectroscopy", *Vibrational Spectroscopy* **65**, 50 (2013).
(3) S. Bawaked, K. Narasimharao, "Structural and catalytic properties of copper silicate nanomaterials", *Scientific Reports* **10**, 1 (2020).

*Speaker

Keywords: infrared spectroscopy, colloidal silica, glass structure, nuclear magnetic resonance spectroscopy