Rev. Cub. Física vol.25 No.2-A (2008) p.67-69
ISSN: 0253-9268. Original paper

Abril 17-19, La Habana

Revista Cubana de Física
Calle I No. 302 e/ 15 y 17
Vedado, La Habana.
www.fisica.uh.cu/biblioteca/revcubfi/index.htm

Hydrophilic character study of silica-gel by a laser dynamic speckle method

C. I. Cabello[a*], G. Bertolini[a], S. Amaya[b], R. Arizaga[b], M. Trivi[b*]

a) Centro de Investigación y Desarrollo en Ciencias Aplicadas Dr. J. Ronco (CINDECA-CCT La Plata-CONICET-UNLP); ccabello@quimica.unlp.edu.ar
b) Centro de Investigaciones Ópticas (CCT-La Plata-CONICET-CIC) y UID Optimo, Dpto. Cs Básicas, Fac. Ingeniería, Universidad de La Plata; marcelot@ciop.unlp.edu.ar
*Members of the research staff of CIC PBA.

Recibido el 1/02/2008. Aprobado en versión final el 4/07/08.

Abstract. This research shows a dynamic speckle application to the hydrophilicity study of commercial silica-gel with different textural properties, i.e. grain size, superficial area and pore volume. The experimental results show the temporary evolution of the speckle patterns from the samples during the water adsorption process. These results show a good correlation with textural parameters.

Sumario. El trabajo muestra una aplicación de la técnica de speckle dinámico al estudio de hidrofilicidad de sílica gel comercial con diferentes propiedades texturales, tales como tamaño de granos, área superficial y volumen de poros. Los resultados experimentales muestran la evolución temporal de los diagramas de speckle durante el proceso de adsorción del agua de las muestras. Los resultados muestran una buena correlación con los parámetros texturales.

Keywords. Silica gel 82.70.Gg; hydrophilic effect 82.70.Uv; textural properties 81.40.Ef; dynamic speckle 42.30.Ms.

1 Introduction

When a laser beam illuminates a rough surface of an object, a typical *speckle pattern*[1] is observed. If the surface of the objects presents some type of local movement, then the observed speckle evolves in time. This *dynamic speckle*[2,3] is characteristic of biological samples and can also be observed in non-biological industrial processes, including the drying of paint, corrosion and heat exchange, etc.

The visual appearance of the speckle diagram is similar to that of a boiling liquid. This activity takes place when the sample changes its properties due to the movements of the scattering centers, changes in the optical path due to variations of refractive index, configuration changes or combination of these situations.

The temporary evolution of the speckle patterns is correlated with the "activity" of the sample and may provide an interesting tool to characterize the parameters involved in these processes.

The present work shows a result of a dynamic speckle application to the hydro-adsorption study of commercial silica-gel with different textural properties, i.e. grain size, superficial area and pore volume. The experimental results show the temporary evolution of the speckle patterns of the samples during the water adsorption process.

2 Materials and methods

For comparative purposes, two types of commercial silica gel with different textural properties were used: low porosity Degussa "aerosil" and higher porosity Merck Kieselgel. Also 20 g of low porosity Degussa aerosil was treated for increasing its porous volume by adding

100 ml of $NH_4(OH)$ (pH = 10.6) aqueous solution. The mixing was stirred for 30 minutes and then the solid was filtered and dried. Textural properties were obtained by BET method[4]. Then the volume of water adsorbed by a known amount from each material until incipient humidity was reached was measured.

Table 1 shows textural properties of several materials: regular and treated aerosil Degussa and Kieselgel Merck.

In addition, a measurement of the adsorption properties of silica was performed by a thermo-gravimetrical analysis (TGA)[5] using a Shimadzu 145 Thermoanalyzer equipment in air atmosphere from room temperature to 500ºC. In this case, 100 mg of different samples were previously soaked in 2 ml of distilled water and weighed, then placed in stove for 1h at 80ºC and weighed again. Finally, TGA measurement was performed.

In the dynamic speckle experiments, 1g of each silica samples was soaked with 1ml of water. The stage of the sample was controlled every two minutes at the beginning of the process and then every five minutes in the final part, the evolution was followed for one hour. Room temperature and humidity: 19°C, 60%.

The dynamic speckle patterns were obtained using an attenuated 10 mW He-Ne laser to illuminate the sample. A CCD camera connected to a personal computer with a frame grabber was used to record the images composed by 512 X 512 pixels and digitized to 256 intensity levels (8bits) taken every 0.08s. Fig. 1 shows the experimental set-up.

Quantitative measurements were employed for the digital data processing. A method to measure the activity of the dynamic speckle is the Temporal History of the Speckle Pattern (THSP) proposed by Oulamara et al[6]. In our case, 512 successive images of the dynamical speckle pattern were recorded. A certain column (for example, the one in the middle) was selected from each of them. Then, a new image, named THSP, was constructed. This one was composed by setting, side by side, the chosen column of the 512 images. While the size of the speckle grain in the spatial (vertical) direction was determined by the wavelength of the light and the numerical aperture of the optical system, the length of the segments in the time (horizontal) direction depended on the phenomenon producing the dynamic speckle. It can be expected that fast phenomena could give rise to many short segments while, conversely, slow phenomena could give rise to long segments.

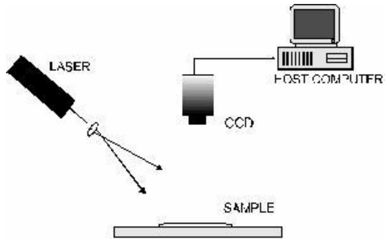
The inertia moment of the co-occurrence matrix[7] is a usual texture descriptor that was used as a measurement of speckle activity in some applications. It is a second order statistical tool based on the measurement of the spread of the number of intensity level variations in time in the THSP.

The co-occurrence matrix (M_{CO}) is defined as:

$$M_{CO} = [Nij] \qquad (1)$$

The entries are the number N of occurrences of a certain intensity value *i*, that is immediately followed by an intensity value *j*. When the intensity does not change, the only non zero values of this matrix belong to the principal diagonal. When the sample shows activity intensity values that change in time, the number of nonzero values outside the diagonal is increased. So the matrix is sparser.

Figure 1. Experimental setup. ▶



A measurement of the spread of M values around the principal diagonal can be constructed as the sum of the matrix values times its squared row distance to the principal diagonal. It is the Inertia Moment (*IM*) of the matrix with respect to that diagonal in the row direction

$$IM = \sum_{ij} M_{ij} (i - j)^2$$

where M_{ij} is the normalized co-occurrence matrix. The normalization consists of dividing all the matrix entries by the number of times when the first intensity *i* appears.

3 Experimental results

In Table 1 it is possible to observe that after the ammonium hydroxide [$NH_4(OH)$] treatment in Degussa silica both superficial area and pore volume increased.

Table 1
Textural properties of different silica

Silica-gel	SBET (m^2/g)	Porous Volume (cm^3/g)
Degussa (Non porous)	65.00	0.138
Degussa (Non porous treated)	180.00	0.766
Merck Kieselgel 60 G (porous)	224.61	0.615

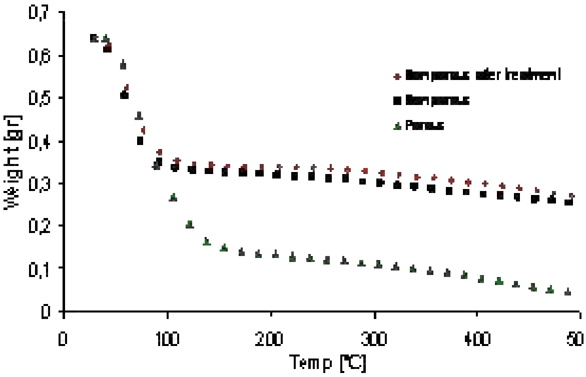


Figure 2. TGA patterns of different silica gel.

Pores can be of different sizes: macro, meso and micropores. In this process, at high pH, the silica-gel surface is basically composed by silanol groups (hydroxil) $SiO_2.OH$, acquiring a great concentration of –OH groups. On the other hand, the NH_4^+ cations, which initially were grouped around anions, were lately eliminated by a soft calcinations process. This thermal treatment provoked the pore formation, then H_2O molecules would be concentrated through hydrogen bridges. Thus, the solid improved its capacity of water adsorption.

The importance of surface silanol (hydroxyl) groups is related to the control of the specific physisorption interactions. Fully hydroxylated silica has a high surface OH concentration. It might be expected that there could be a simple correlation between the surface OH concentration and the affinity for water.

The level of surface OH concentration has a very strong effect on specific interactions that become significant when the adsorptive molecules are quadrupolar (e.g. nitrogen and carbon dioxide) and even more when hydrogen bonding is involved (e.g. with water or the lower alcohols)[8].

There is a general agreement that the removal of surface silanols by heat treatment causes a dramatic reduction in the level of water adsorption whose nature depends on the thermal pre-treatment.

Experimental results of TGA in the temperature range from room temperature to 500 ºC are shown in Fig 2. The process of silica $[SiO_2.(OH).nH_2O]$ dehydration occurred at ~ 70ºC. In the temperature interval from 20 to 180 ºC, silica lost water molecules which desorbed completely from macro, meso and micropores. After this process only silanol groups $[(SiO_2.(OH)]$ were present and the process of dehydroxylation continued up to 500 ºC.[9] Water evaporation was indicated in the TGA experiment by the weight loss of samples. This is a strong effect on the higher area and porosity Merck Kieselgel.

Conversely, in regular and treated aerosil Degussa, TGA showed similar behavior and did not allow separating their patterns according to their adsorption properties. In this case, TGA method was not accurate enough.

In Fig. 3, experimental results of the quantitative *IM* speckle activities are plotted vs. the time of the water adsorption. The initial activity has been normalized for the three specimens.

It can be observed the different behavior of regular and treated Degussa aerosil and Merck Kieselgel. Higher specific area (Merck Kieselgel) material showed a sharp fall in a short time and then a low speckle activity was preserved. Conversely, the lower SBET material (regular Degussa aerosil) showed an initial slight fall, which kept a high speckle activity. The treated material (treated Degussa aerosil) showed an intermediate behavior. These results suggest a correlation of the speckle activity with hydro-adsorption process according to the textural properties of the samples.

4 Conclusions

A dynamic speckle technique was employed in the hydrophilic character study of commercial silica-gel with different textural properties. The experimental results show the temporary evolution of the speckle patterns from the samples during the water adsorption process. This technique enables the comparison between a variety of products and an eventual correlation with textural parameters.

The preliminary results presented in this work suggest that the dynamic speckle could be a good tool to compare the performance of different types of silica-gel. In our case, the dynamic speckle method is more sensitive than the TGA technique.

Besides, this analysis can be considered as a potential new method to study different porous materials of interest such as adsorbents or catalysts supports.

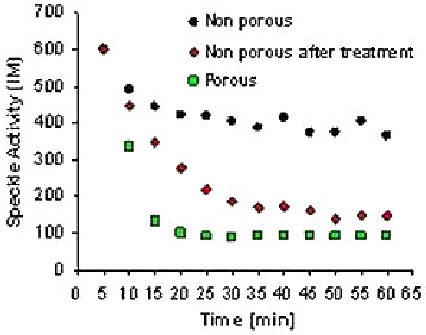


Figure 3. IM speckle activities plotted vs. time of the water adsorption for different silica gel.

Acknowledgements

This work was supported by CONICET, SECyT, CICPBA and UNLP, Argentina.

References

1. J. C. Dainty Laser Speckle and Related Phenomena, Ed., Springer Verlag, Berlin (1975).
2. Y. Aizu, T. Asakura “Biospeckle” Trends in Optics, A. Consortini, Ed., Chap. 2 Academic Press, San Diego, (1996).
3. R. Arizaga, N. Cap, H. Rabal, M. Trivi, Optical Eng. 41, 287-294 (2002).
4. Brunauer, Emmett and Teller (BET) method in "Introduction to characterization and testing of catalysts", J.R.Anderson y K.C.Pratt Ed. Academic Press Australia (1985).
5. D. A. Skoog, J. J. Leary “Análisis instrumental” 4a Ed. McGraw-Hill, Madrid (1994).
6. A. Oulamara, G. Tribillon, J, Duvernoy, J. Mod. Opt. 36: 165-179, (1989).
7. R. Arizaga, M. Trivi, H. Rabal, Optics Las. Tech. 31, 163-169 (1999).
8. F. Ronquerol, J,Ronquerol and K. Sing in “Adsorption by powders and porous solids, Principles, Methodology and Applications”. Eds. Elsevier (1999).
9. U.B. Mioc, S. K. Milonjic, D. Malovic, V. Stamenkovic, Ph. Colomban, M.M. Mitrovic, R. Dimitrijevic. Solid State Ionics 97, 239-246 (1997).