THE CLUSTER MODEL: A HIERARCHICALLY-ORDERED ASSEMBLAGE OF RANDOM-PACKING SPHERES FOR MODELLING MICROSTRUCTURE OF POROUS MATERIALS

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ABSTRACT

A new structural model based on the premises widely used for describing the structure of random porous materials, and especially aerogels, is introduced. Aerogels are described as an assemblage of randomly-packed spheres in several hierarchically-ordered levels. A new algorithm has been developed for constructing structural models from these premises using computer simulation. Subsequently, several techniques for characterising real systems have been simulated, and textural parameters of the models have been obtained, including specific surface area, specific porous volume and the apparent density of the systems, based both on the Monte Carlo technique and on geometrical considerations. This characterisation process yields a set of parameters used for testing the capacity of the models to reproduce the structure of several real systems, like aerogels. Special attention has been paid to the Pore Size Distribution calculations: the Monte Carlo Integration and the Triangulation algorithms have been compared.

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KEYWORDS: Aerogels A120; (Cluster Model, Structural modelling, computer simulation, triangulation method, Monte Carlo, porous materials, Pore Size Distribution)

1. Introduction

Silica aerogels are chemically inert, highly porous, nano-structured materials, synthesized by the well-known sol-gel method [1], and dried by the supercritical drying process conceived by S. Kistler [2] for preventing cracking. In this way we obtain the silica aerogels, more porous materials than the conventionally-dried gels, which are also known as xerogels. Their particular structure is responsible for the most interesting properties of the aerogels, such as low thermal conductivity and very high specific surface area, which can reach values of around 1000 m^2/g or more. Incidentally, an aerogel is currently the solid with the lowest density ever synthesized [3], with a value of 1.9 mg/cm^3. The structure of aerogels has been described as an assembly of randomly-packed spherical particles in several hierarchically-ordered levels [4,5,6,7]. Knowledge of the aerogel structure has been acquired using computer simulation techniques taking inputs from several sources, such as the understanding of the sol-gel process, and the relationship between the structure and the mechanical properties. The structure formation process has been studied using the Molecular Dynamics Technique [8]; this was first applied by Garofalini to the sol-gel process in 1994 [9] using the Feuston-Garofalini potential [10], and he concluded that the structure formation starts with a slow growth process of the individual clusters, followed by the faster growth of the structure due to cluster-cluster aggregation.

It is generally admitted that the Cluster-Cluster Aggregation regimes (DLCA – Diffusion limited Cluster Aggregation, RLCA – Reaction Limited Cluster Aggregation) describe quite well the typical structures obtained via sol-gel. One of the goals pursued most by researchers is to reproduce the formation and growth processes of the aerogels, using the RLCA or DLCA algorithms or some modifications of these [11,12]. Scherer *et col*. [13] used structures generated with DLCA-modified algorithms, characterising them by their fractal dimension, to achieve the power law exponent and they have presented some models to explain the relationship between structure and mechanical properties [14,15]. Then Woignier *et col*. introduced a new technique for characterising these porous systems [16,17], and

concluded that pore size distribution and hydroxyl content are relevant for understanding the mechanical properties of these materials [18]. In a previous study, Woignier and Phallipou proposed one approach starting from a cubic structural model [19] and for a rigid assembly of cohesive spheres [20]. Emmerlig and Fricke also studied this problem, for elasticity and conductivity, through the scaling properties obtained by their simulated aerogel structures [11]. The Cluster Model that is introduced here has also been applied as an initial approach to the study of mechanical properties [7].

Computer simulation techniques have been used to characterise models from several points of view. On the one hand, there are some simulation techniques for studying the texture (specific surface, apparent density, porous volume, porosity...). Gelb and Gubbins have directed their work towards the development of characterisation applications based on the Monte Carlo (MC) technique, for the porous structures generated by simulation [21] and also for testing the validity of the BET [22] or the BJH [21] methods for analysing the adsorption/desorption isotherms. A. Hasmy has also worked on characterisation, studying the behaviour of the characteristic cluster size and the influence of the simulation box size [23]. One of the most frequently studied features of porous materials is the Pore Size Distribution (PSD), which is experimentally calculated by several techniques, such as N_2 adsorption or Hg porosimetry [24]. Similarly, the PSD of different porous structural models has been also pursued by several research groups, using different strategies or different concepts of what constitutes a pore [16,25,26,27].

We have also applied our models to simulate titania (TiO_2) porous systems. These are widely used in the field of photocatalysis and new-generation photovoltaics [28]. The use of mesoporous morphology allows for a very high light-harvesting efficiency due to the large internal surface area of the material [29]. Furthermore it has been observed that transport and recombination in mesoporous solar cells is limited by point defects located on the surface of the titania nanoparticles [30]. For this reason it is of considerable practical interest

to have a theoretical estimation of the surface area as a function of parameters like the particle size or the apparent density

2. The Cluster Model: algorithm and characterization techniques.

We are proposing a new algorithm based on the premise of randomly-packed spheres in several hierarchically-ordered levels for building the Cluster Models. The aim of this technique is to build structural models emulating the real systems. Its best quality is its versatility: by tuning the geometric parameters of the model we can obtain very different assemblies of randomly-packed spheres for representing very different porous systems. The main structural parameters in this model are the elementary particle radius, the number of hierarchical levels and the mean contact distance and shell radius of each level. However, models constructed by this procedure are intended to describe not the growth process of real systems, but the final state of such systems. They are categorised as static models [31]. FORTRAN 90 programming language on a Pentium 4 (3.5 GHz) processor running under *Linux Ubuntu* OS was used; while only a few seconds was taken to construct these systems, several hours were spent in characterising them. In the course of this article, the particle diameter has been used for convenience to denote each of the models.

2.1 Algorithm

¡Error! No se encuentra el origen de la referencia. displays a diagram explaining the building process. The algorithm works as follows: first we place one *elementary* sphere in the centre of our system. Then we randomly place as many other spheres as are needed to cover fully the surface of the first one; this produces the first random shell. Every sphere has to be *in contact* at least with one other; that is, it must be at a previously defined distance. One can build as many shells of random spheres as are required. Then the *basic aggregate* of the first hierarchical level is built, and its diameter is measured. This diameter will be taken as the diameter of a *secondary sphere*.

The following hierarchical level is built in the same way, taking the basic aggregate as if it were an elementary sphere, that is, building this next level with more *secondary spheres*. After building this new aggregate, each secondary sphere is replaced with one basic aggregate, to obtain a two-level hierarchically-ordered assembly of randomly packed spheres. Then, the size of this system is measured again and is taken as the diameter of a *tertiary sphere*, if the intention is to build a third hierarchical level. An aggregate of *tertiary spheres* can then be built and, lastly, each *tertiary sphere* is replaced by the two-level system; in this way a three-level hierarchically-ordered system is obtained. This process can be repeated as many times as required. Typical values of our models are 1000 to 60,000 particles organised in 2 to 4 shells of random-packed spheres and 2 or 3 hierarchical levels; their contact distance d usually is found in the interval $0.85D < d < 1.0D$, D being the particle diameter.

Although auto similarity is potentially present in the Cluster Model as a consequence of its generation algorithm, in the present case we have not considered a fractal description because the structure of target aerogels is not auto similar over more than one order of magnitude. In the future we will emulate the fractal structure of those aerogels that present a well-defined fractal dimension.

Cubic simulation boxes have been used for the characterising applications that are boundary-dependent and finite size-dependent, to apply periodic boundary conditions. One of the main topics previously dealt with is the question regarding the finite size effect. To be absolutely certain that one is working under enough repetitive conditions from the point of view of desired results, it is important to work always above the minimum representative size, to ensure that the results of the simulation are not determined by the size of the simulated system, that is, one should work with what has been called the Representative Volume Element [32]. To evaluate this feature, we tested the porosity, as this parameter is very easy and quick to calculate, and it presents a rapid convergence as the system size

increases [33]. It was confirmed that, for models with a system size above 8D, the values were within the statistical error. Therefore we always worked with systems larger than 8D.

2.2 Previous structural models

The starting point for this algorithm is the previous structural model for gels proposed by J. Rodríguez-Ortega and L. Esquivias [26,34]. These authors developed an algorithm for randomly-packed spheres and they characterise systems by geometrical considerations. The main advantage of this algorithm is that it always works with reduced units, so results are independent of particle-size. The most important objective is to obtain the Pore Size Distribution. Each system yields a unique PSD, so this curve can be used to match real systems to their corresponding structural models.

2.3 Texture

The specific surface and volume, the porosity and the apparent density can be calculated by various simulation techniques or through geometrical considerations, as has been explained in a previous study [7]. This set of parameters is the main indicator used to match a Cluster Model to a real system. Thus, we built several Cluster Models, and tuned the formative parameters in order to reproduce real values of texture, PSD, etc. We have applied the improved version of the pore volume calculation proposed by S. Gavalda [35] who explained that this value was being systematically underestimated. We took several real systems [ ] and built their respective Cluster Models, characterising them through the usual simulation techniques previously cited. Most of the parameters are purely geometric, but others, like apparent density, needed the value of the skeleton density. We preferred to use the calculated value of the skeleton density of aerogels of 2.09 g/cm^3 [36] rather than the more usual value of 2.2 g/cm^3, from bulk silica, used in other simulations.

2.4 Pore Size Distribution

There are several possible methods for obtaining the PSD of any structural model built from elementary spheres. It is generally accepted that a pore can be understood as a spherical set of points representing the pore volume, so the PSD is usually constructed by considering

for each point of the pore space, the radius of the biggest sphere that can be placed in the pore volume, centred on the given point and without overlapping the solid phase [25].

An advance on this method was made by Gavalda and Gelb, who calculate the PSD by the technique known as MC integration [21,37]. For any given point in the pore space, they looked for the largest sphere that can be placed in that space without overlapping the solid phase, but now not restricted to being centred on the given point, merely containing that point. In this way, more irregularities of the pore shape are taken into consideration for the measurement, so pore space is more fully described.

Rodriguez-Ortega (RO) worked with another concept for obtaining the PSD, by testing for the maximum size of spheres that the pore space can notionally hold, based on previous works by Finney and Wallace [38]. For each set of four elementary spheres in mutual contact, not necessarily tangentially, the largest sphere that the pore space between them can contain is obtained. Again, the pore shape description is improved when spheres are used as the basic tool.

In the Triangulation method (TR) of J. Primera [16] no previous assumption is made in respect of the pore shape. This is a new technique that allows the pore size distribution to be measured by means of a triangulation of the pore space. In this method numerous 2-dimensional cross-sections of the pore space are studied. For each cross-section, a two-dimensional TR method is applied to the “space” of the pore. A schematic illustration of this method is shown in **¡Error! No se encuentra el origen de la referencia.**. First, a large number of points are randomly located in the pore space and then the TR procedure is applied at each point.

This method of describing the pore space gives a more realistic result as it does not require any previous assumption of the shape of the pore, but considers all possible different shapes, not only the spherical.

3. Results

3.1 Emulating real systems

We have built several cluster models that represent the microstructure of various real systems. Initially, the aim of these models was to emulate the structure of the porous silica aerogels, but in fact, they can be used to emulate a variety of disordered particulate materials which could be described as randomly-packed spheres. **¡Error! No se encuentra el origen de la referencia.** gives the characterization parameters of some real systems and their corresponding models.

As mentioned in the introduction, we have made use of our models to study mesoporous TiO_2 systems films for photovoltaic applications in Dye Sensitised Solar Cells. These films have apparent densities of around 1 g/cm^3 and porosities of around 50% [39]. Taking into account that usually the active surface in a solar cell is 1000 times the external surface of the cell, for a typical cell of around 1 cm^2 area and 50 microns thickness, a specific surface of 20 m^2/g is obtained.

Systems #1 and #2 correspond to two different silica aerogels prepared from TEOS, and were characterized by the analysis of the N_2 adsorption/desorption isotherms [40]. System #3 corresponds to the porous TiO_2 usually used in solar cells. The object of this part of the work was to construct models corresponding as accurately as possible to the real systems. A very good correspondence can be seen between the real systems and their cluster models. Taking the experimental structural parameters, the models presented reproduce the textural values of the real systems.

A sketch of a cluster model can be seen in **¡Error! No se encuentra el origen de la referencia.** rendered using the free software POVRay [41]. The system illustrated corresponds to the simulation box cropped from model #2, and has around 3000 particles.

3.2 Pore Size Distribution

In order to ensure the consistency required between the RO [26] and Cluster models, we performed some simple simulated experiments, obtaining the PSD by the MC Integration of a Cluster Model as if it were a real system, and using it to look for the matching RO model. Then, the parameters of the two models were compared. The resulting curves and the

geometrical parameters are shown in **¡Error! No se encuentra el origen de la referencia.**, Upper and **¡Error! No se encuentra el origen de la referencia.** respectively.

With regard to the different techniques for calculating the Pore Size Distribution, we have compared the resulting curves obtained by two different methods: the widely used MC Integration, and a relatively new approach, the TR method. For a given cluster model, we applied the two methods to obtain the two PSD curves, which are shown in **¡Error! No se encuentra el origen de la referencia.** Lower. The TR curve was taken from 25 2-dimensional cross-sections of the pore space at each of more than 15.000 points taken from a grid of the total porous space. Both the curves were obtained by averaging at least 5 replicates.

Results show that the curve obtained by TR presents more noise, whereas MC gives a smoother PSD. Moreover, TR yields larger pore sizes and a size distribution centred on around 0.8D. It also indicates the presence of pores of around 0.5D and 1.1D, whereas MC gives just one typical size for the pore space of around 0.16D.

4. Discussion

Geometrical parameters of selected models reproduce quite well those values reported from experimental measurements. There is evidently good agreement on the particle size of 1.1 nm for elementary particles reported in the literature [36,40] and that obtained through modelling. The apparent densities and specific surface data obtained for TiO_2 are close to the values determined experimentally for this type of system. In fact, roughness factors (ratio of the surface to the volume) ranging between 57 and 149 μm^{-1} are found by gas sorption experiments [30]. Our predictions are 43 and 35 μm^{-1} for the models of 15 and 20 nm particle radius, respectively. Furthermore, the theoretical results predict a decrease of the roughness factor with the size of the particle, in complete agreement with the experimental findings [30].

4.2 Pore Size Distribution

Regarding the consistence between the cluster models and their predecessors, the RO models, good agreement can be found between the two sets of textural parameters [**¡Error!**

No se encuentra el origen de la referencia.], those of the “real” system obtained from the Cluster Model via MC and those from the fitted RO model. The corresponding RO model was found by fitting the peak and the shape of the curve [**¡Error! No se encuentra el origen de la referencia.**, Upper]. As each RO model describes just one hierarchical level, the absence of fit on the left side of the PSD, regarded as the microporosity, reveals the existence of two hierarchical levels. The selected model satisfactorily describes the mesoporous structure (~2nm pore radii), so in order to make a complete description of the PSD, another RO model should be considered for describing the microporous structure. Therefore, on the one hand, this result is consistent with the real structure, thus supporting the consistence between the two models, but on the other hand, this fact implies that reported RO textural values are relatively underestimated.

Considering the comparison between MC and the TR curves of the PSD obtained from the same cluster model [**¡Error! No se encuentra el origen de la referencia.**, Lower], it can be seen that TR finds larger pores than MC. The lack of constraints of the TR method enables it to give a more realistic description of the pore space. **¡Error! No se encuentra el origen de la referencia.**5 illustrates diagrammatically a 2 dimensional pore between 4 spheres. In the pore *space* (white) several test points have been positioned in the form of a grid. It can be clearly seen that all the 13 test points belong to the same connected pore space. However, a technique that considers the pore as the largest test sphere that can be centred on a test point without overlapping the solid phase will yield 4 different pore sizes. If movements of the centre of the growing test sphere are allowed as in MC Integration, we will obtain a bimodal PSD, one size corresponding to the radius of the circle containing, for example, point 2 in the diagram, and the other size corresponding to the radius of the maximum circle tangential to the four circles representing solids, which contains the remaining 9 points. In contrast, the RO and TR methods will yield a monomodal PSD for this connected pore space. RO will find the same four closest spheres for all the 13 points, and with TR, because even the most

“interstitial” points like #3 in **¡Error! No se encuentra el origen de la referencia.**5 almost penetrate the whole pore space, the 13 points will also yield the same pore radius.

5. Conclusions

The new algorithm that has been introduced is a very useful tool for modelling the microstructure of random materials. The parameters of these models can be easily tuned to match the values of a variety of porous systems, as it has a very versatile geometrical construction. Cluster models have been used to model very different porous systems, to give an interesting illustration of the microstructure.

The models provide a straightforward and precise computation of the internal surface of titania mesoporous films, a parameter of great importance in the performance of Dye Sensitised Solar Cells.

These new models are consistent with their predecessors, as can be deduced from the comparative study performed in this study. Different models, giving a similar texture, have the same Pore Size Distribution curve.

Several techniques for obtaining the Pore Size Distribution have been compared and the different concepts of what constitutes a pore are also discussed. The triangulation algorithm yields a more realistic pore space description, especially in comparison with the Monte Carlo integration technique. Hence the consideration of the pore as a sphere may not be adequate for describing the real pore space.

6. Acknowledgements

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FIGURE AND TABLE CAPTIONS:

¡Error! No se encuentra el origen de la referencia.**:** Diagram of the Cluster Model algorithm.

¡Error! No se encuentra el origen de la referencia.: Schematic illustration of the two-dimensional triangulation method applied to the pore space. Points 1, 2 and 3 correspond to the three vertices of one of the triangles.

¡Error! No se encuentra el origen de la referencia.: Sketch of a Cluster Model, corresponding to the simulation box cropped from system #2 of table #1 (Colour online).

¡Error! No se encuentra el origen de la referencia., Upper: Pore Size Distributions (PSD) of two different systems: a Cluster Model (CM) and the corresponding fitted model of Rodríguez-Ortega (RO). The CM curve was averaged over at least five replicates. Lower, Comparison of the PSD of a system constructed by the Cluster Model Algorithm, calculated using two different techniques: the Monte Carlo (MC) Integration and the Triangulation method (TR).

¡Error! No se encuentra el origen de la referencia.5: 2D diagram of a grid in the pore space between 4 spheres.

Table 1: Structural parameters of several real systems and the geometric and structural parameters of their corresponding counterpart cluster models.

Table 2: Textural parameters of both models: the Cluster Model and the model of Rodríguez-Ortega.

FIGURES

Figure 1

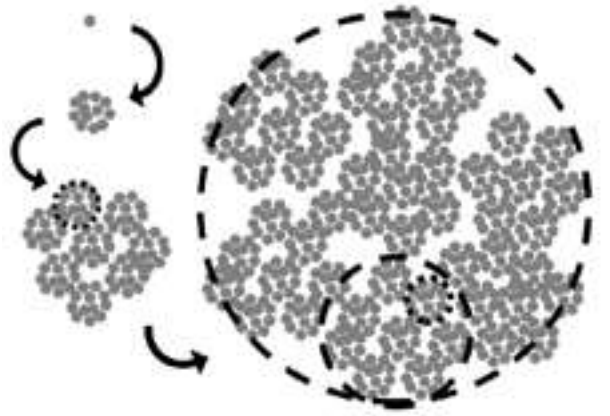


Figure 2

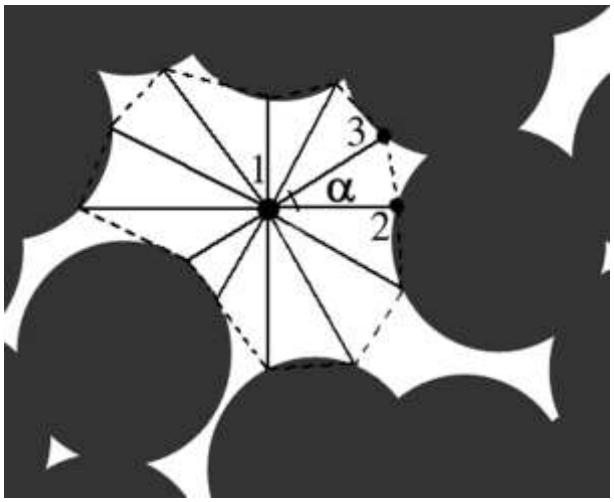


Figure 3:

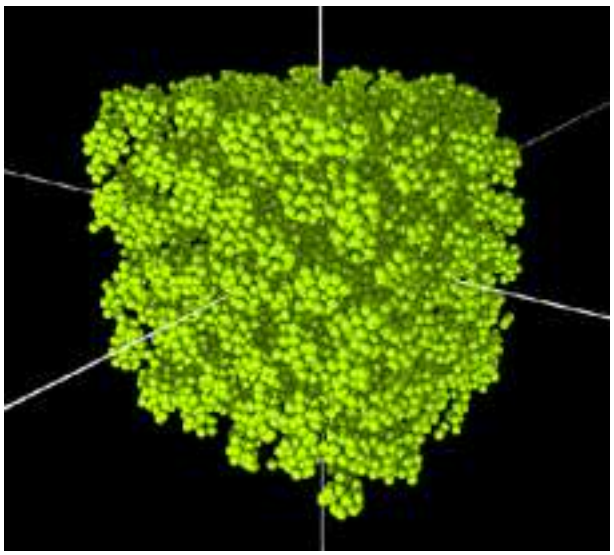


Figure 4:

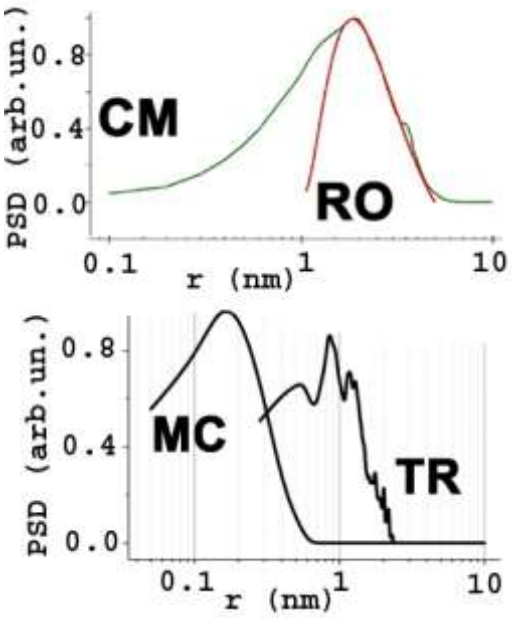
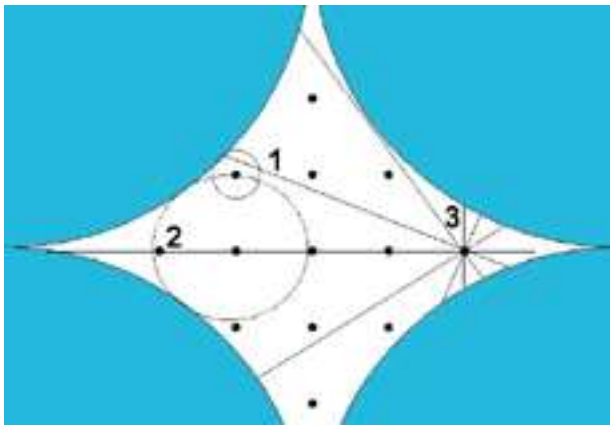


Figure 5:



TABLES:

Table 1:

System 1 **(pure silica aerogel)** *Apparent density: 0.83 g/cm^3* *Specific surface: 387-407 m^2/g* *Specific porous volume: 0.73-0.74 cm^3/g*	**Model 1** *Apparent density: 0.80 g/cm^3* *Specific surface: 384 m^2/g* *Specific porous volume: 0.72 cm^3/g*
System 2 **(pure silica aerogel)** *Elemental Sphere radius: 1.2 nm* *First aggregate radius: 4.5 nm* *Specific surface: 640 m^2/g*	**Model 2** *Elemental Sphere radius: 1.1 nm* *First aggregate radius: 4.5 nm* *Specific surface: 612 m^2/g*
System 3 **(mesoporous TiO_2)** *Radius: 5-25 nm* *Apparent density: 1 g/cm^3* *Specific surface: 20 m^2/g*	**Model 3** *a) Radius: 15 nm* *Apparent density: 0.93 g/cm^3* *Specific surface: 46m^2/g* *b) Radius: 20 nm* *Apparent density: 1.09 g/cm^3* *Specific surface: 32 m^2/g*

Table 2:

Cluster Model	**Model of Rodriguez-Ortega**
Apparent density: 1.11± 0.06 g/cm^3 *Porosity: 54±3%* *Specific porous volume: 0.49±0.06cm^3/g*	*Apparent density: 1.06 g/cm^3* *Porosity: 52%* *Specific porous volume: 0.48 cm^3/g*

REFERENCES

1 J. Brinker and G. Scherer, "Sol–Gel Science: The Physics and Chemistry of sol–gel Processing." Academic Press, San Diego, CA, 1990.
2 S. Kistler. *J.Phys.Chem.* 36 (1), (1932) 52.
3 Lawrence Livermore National Laboratory: http://www-cms.llnl.gov/s-t/aerogels_guinness.html. Last visit, 23/nov/2006.
4 J. Zarzycki, *J. Non-Cryst. Solids* 121 (1990) 110-118.
5 J. Zarzycki. *J. Non-Cryst. Solids* 147&148 (1992) 176-182.
6 L. Esquivias, J. Rodriguez-Ortega, C. Barrera-Solano, N. de la Rosa-Fox. *J. Non-Cryst. Solids.* 225 (1998) 239-243.
7 V. Morales-Florez, N. de la Rosa-Fox, M. Piñero and L. Esquivias, *J of Sol-Gel Sci. and Tech.* 35, (2005) 203-210.
8 K. Yamahara, K. Okazaki. *Fluid Phase Equilibria* 144 (1998) 449-459.
9 S. H. Garofalini, G .E. Martin. J. Phys. Chem. 98 (1994) 1311-1316.
10 B. P. Feuston, S. H. Garofalini. *J. Phys. Chem.* 94 (1990) 5351-5356.
11 A. Emmerling, J. Fricke. *J. Sol-Gel Sci. and Tech.* 8 (1997) 781-788.
12 M. Grzegorczyk, M. Rybaczuk, K. Maruszewski. *Chaos, Solitons & Fractals* 19 (2004) 1003-1011.
13 H. Ma, J. H. Prevost, G. W. Scherer. *International Journal of Solids and Structures* 39 (2002) 4605-4614.
14 H. Ma, A. P. Roberts, J. H. Prevost, R. Jullien, G. W. Scherer. *J. Non-Cryst. Solids* 277 (2000) 127-141.
15 H. Ma, J. H. Prevost, R. Jullien, G. W. Scherer, *J. Non-Cryst. Solids* 285 (2001) 216-221.
16 T. Woignier, J. Reynes, A. H. Alaoui, I. Beurroies, J. Phallipou, *J. Non-Cryst. Solids* 241 (1998) 45-52.
17 J. Primera, A. Hasmy, T. Woignier, *J. Sol-Gel Sci. and Tech*. 26 (2003) 671-675.
18 T. Woignier, F. Despetis, A. Alaoui, P. Etienne, J. Phalippou, *J.Sol-Gel Sci. and Tech.* 19 (2000) 163-169.
19 T. Woignier, J. Phalippou, *J. Non-Cryst. Solids* 100 (1988) 404-408.
20 A. Rumpf, *Chem. Ing. Tech.* 30 (1958) 144.
21 L. D. Gelb, K.E. Gubbins, *Langmuir* 15 (1999) 305-308.
22 L. D. Gelb, K. E. Gubbins, *Langmuir* 14 (1998) 2097-2111.
23 A. Hasmy, R. Jullien, *J. Non-Cryst. Solids* 186 (1995) 342-348.
24 L. Esquivias, V. Morales-Florez, M. Piñero, N. de la Rosa-Fox, *J. Non-Cryst. Solids* 351 (2005) 3347-3355.
25 S. Torquato, "Random Heterogenous Materials". Springer-Verlag New York, Inc, 2002.
26 Julián Rodríguez Ortega, Modelos de estructura de geles densos (Models of structure of dense gels), Ph.D. thesis, Universidad de Cádiz, Spain (1996).
27 K. T. Thomson, K. E. Gubbins, *Langmuir* 16 (2000) 5761-5773.
28 16th International Conference on Photochemical conversion and Storage of Solar Energy, Uppsala, Sweden, July 2-7, 2006.
29 M. Grätzel, Nature, 414, (2001) 338.
30 N. Kopidakis, N. R. Neale, K. Zhu, J. van de Lageemat and A. J. Frank, Appl. Phys. Lett. 87 (2005) 202106.
31 L. T. To, Z. H. Stachurski. *J. Non-Cryst. Solids* 333 (2004) 161-171.
32 G. Cailletaud, S. Forest, D, Jeulin, F. Feyel, I. Galliet, V. Mounoury, S. Quilici. *Computational Materials Science* 27 (2003) 351-374.
33 J. Primera Ferrer, Ph.D. thesis, Université Montpellier II, France (2002).
34 J. Rodriguez-Ortega, L. Esquivias, Journal *of Sol-Gel Science and Technology* 8 (1997)117–123. (1997)
35 S. Gavalda, K. Kaneko, K. T. Thomson, K. E. Gubbins, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 187–188 (2001) 531–538.
36 L. Esquivias, M. C. Barrera-Solano, N. de la Rosa-Fox, F. L. Cumbrera, J. Zarzycki, in *Ultrastructure Processing of Advanced Materials,* edited by D. R. Durham and D. R. Ulrich (John Wiley & Sons, Inc., 1992), p315.
37 S. Gavalda, K. E. Gubbins, Y. Hanzawa, K. Kaneko, K. T. Thomson, *Langmuir* 18 (2002) 2141-2151.
38 J. L. Finney, J. Wallace, *Journal of Non-Crystalline Solids* 43 (1981) 165-187.
39 J.A. Anta, F. Casanueva, G. Oskam, *J. Phys. Chem. B* 110 (2006) 5372.
40 M.C. Barrera-Solano, N. de la Rosa-Fox and L. Esquivias. *J. Non-Cryst. Solids 147/148* (1992) 194-200.
41 Persistence Of Vision, www.povray.org. Last visit, 23/nov/2006.