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Ultrasound as a tool for the preparation of gels: effect on the textural properties of TiO_2–SiO_2 aerogels

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TiO_2–SiO_2 aerogels have been prepared by hydrolysis and polycondensation of alkoxides following two different methods: the classic one, using ethanol as a solvent, and the sonic one, by means of activation with ultrasound. The work is focused on the comparison of the textural properties of gels obtained by both synthetic routes. Nitrogen physisorption, mercury pycnometry and transmission electron microscopy have been used as characterization techniques. The sonogels present higher values of specific surfaces and apparent densities, lower pore volumes, finer and sharper pore-size distributions and lower average particle size. These properties are discussed and related to the preparation techniques.

1. Introduction

In recent years, ultrasound has found many new applications in chemistry. According to recent reviews on the subject [1, 2], interest in using ultrasound has been established for synthesis reactions in aqueous and organic solvents, in the formation of reactive emulsions from immiscible liquids, and in reactions involving solids immersed in a liquid or gas phase.

Ultrasound provides a form of energy which can modify the chemical reactivities in a different way to other conventional sources such as heat, light or pressure. The collapse of micro bubbles generated by sonicating a reactive system with ultrasound produces local increases of pressure and temperature as high as several hundred bars and several thousand Kelvin [3], thus providing new routes for the occurrence of chemical reactions.

One of the problems with which ultrasound has proved useful is the preparation of gels by hydrolysis and polycondensation of alkoxides. The classic procedure for the sol–gel synthesis of high-purity glasses and ceramics starts from a mixture of alkoxides and water in a common solvent, usually an alcohol. These reagents are allowed to react until a gel is obtained. Tarasevich [4] proposed an alternative route for the obtention of silica gels, in the absence of a solvent, by means of ultrasonic activation. This procedure has been extended to the preparation of multicomponent systems such as P_2O_5–SiO_2 [5, 6] and TiO_2–SiO_2 [7, 8]. Materials obtained in this unconventional way have been called sonogels.

The present paper reports a comparative study of the textural properties of TiO_2–SiO_2 aerogels obtained by the classic method (C) and the sonogel route (S). Several TiO_2 loadings (1, 5 and 10 mol %) were considered in the work. The study was carried out using the results of nitrogen adsorption experiments, apparent density measurements by mercury pycnometry, and transmission electron microsocpy (TEM).

The TiO_2–SiO_2 systems have been selected because of their current interest as advanced glasses [9, 10] and catalytic materials [11, 12].

2. Experimental procedure

Tetraethoxysilane (TEOS) and tetrabutylorthotitanate (TBOT) were used as precursors for the preparation of gels. Because TBOT is very reactive with water, it was modified by addition of acetic acid (HAc) as described elsewhere [13]. The selected HAc/TBOT molar ratio was 5.5. *n*-Butanol (BuOH) was also added with a BuOH/TBOT molar ratio of 3.5. The H_2O/TEOS ratio was 4 for all the prepared gels. Hydrochloric acid, at $pH = 2$, was present as a catalyst in the hydrolysis water.

The sonogels were prepared as follows: 40 mm diameter glass beakers containing 20 ml TEOS–H_2O mixtures were exposed to the action of ultrasound produced by a sonifier (Vibracell Sonics Materials, USA) operating at 20 kHz, with a titanium transducer of 13 mm diameter. The tip of the sonifier was introduced into the reactive mixture. After about 10 min a foaming effect was observed, the liquid turned homogeneous and ethanol vapour evolution could be detected. At this moment irradiation was stopped, the beaker was cooled to 273 K, and appropriate amounts of the BuOH–HAc–TBOT solution were added under vigorous stirring. After mixing, the liquids were transferred to hermetic glass containers and stored in an oven at 323 K. Gelling times decreased for increasing TiO_2 loadings, ranging from 40–90 min.

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Classic gels were obtained by mixing the TEOS–H_2O mixtures with the solution containing the modified TBOT precursors, in the presence of 50 vol% ethanol. Gelling took place in hermetic glass containers, at 323 K, after periods of time ranging between 1 and 5 days.

The sono and classic gels were aged for 1 week at 323 K. Finally, aerogel monolithic pieces were obtained following autoclave drying treatments under hypercritical conditions [14] (pressure 150 bars, and 573 K).

A conventional volumetric high-vacuum glass system, giving an ultimate vacuum better than 10^{-6} torr, (1 torr = 133.322 Pa), equipped with a MKS Baratron BHS1000 pressure transducer, was used to carry out the nitrogen physisorption experiments at 77 K. The amount of sample selected for each measurement was 100 mg. The samples were outgassed at 500 K for 3 h thus giving a residual vacuum better than 10^{-5} torr.

The apparent densities of the aerogels were measured volumetrically by mercury pycnometry. The mercury pressure over the samples in these experiments was 1.1 bar. Transmission electron microscopy (TEM) was carried out for 5 % TiO_2 loading samples. A Jeol 1200 EX equipment was used for the study. Samples were gently ground in a mortar to obtain powders which were further dispersed on holey carbon grids.

3. Results

An experimental study of the adsorption and desorption branches of the nitrogen isotherms was carried out for the six TiO_2–SiO_2 aerogel samples. These samples will be referred as xS or xC, where x is the titania mole per cent, and S and C take account of the sono- or classic character of the preparation, respectively.

All the isotherms can be classified as corresponding to type IV [15]. Fig. 1 shows the plots of the isotherms of 5S and 5C samples, which can be considered as representative examples of the characteristic behaviour of sono and classic aerogels. Both types present saturation effects although they are much more pronounced for the S series. Hysteresis loops are also observed in all cases, thus indicating the existence of a well-developed mesoporous texture (pore radii higher than 1.0 nm and lower than 50.0 nm). The shape of the hysteresis loops agrees with type H1 of the IUPAC classification for the classic gels, and with type H2 for the sonogels [16].

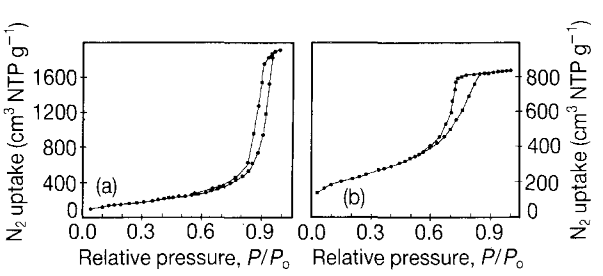

Figure 1 Representative nitrogen physisorption isotherms of C and S type samples. (a) 5C, (b) 5S.

In the range of relative pressures lower than 0.30, the experimental data can be adjusted with excellent agreement to the well-known BET equation (linear correlation coefficients better than 0.999). This method allows estimation of the specific surface areas of the aerogels. The BET surface areas of the S-type samples range between 704 and 774 $m^2 g^{-1}$, while C samples show lower values, ranging between 465 and 598 $m^2 g^{-1}$, Fig. 2. The fitting to the BET equation also led to the obtention of the C parameter (15), the values of which fell between 47 and 150. This range of variation suggests that following the BET method, reliable values of surface area can be deduced.

The t method has been applied in order to check the existence of microporosity in the aerogels (pore radii lower than 1.0 nm). Standard t values used in this study have been taken from the literature [17]. The plots representing nitrogen uptake versus t, shown in Fig. 3 for Samples 5C and 5S, can be fitted to straight lines passing through the origin for t values lower than 1.2 and 0.6 nm, respectively. These results indicate that, according to this method, no microporosity could be detected in any of these samples. Other C and S samples behave in a similar way to the 5% TiO_2 aerogels. The data shown in Fig. 3 are also indicative of the existence of smaller sized mesopores for S-type samples, because deviation of the linear pattern appears at lower t values. However, sonogel t plots show a constant uptake for t values higher than 1.3 nm (1S and 5S) or 1.7 nm (10S), thus indicating that pores of these samples are filled with adsorbate at relatively low pressures. This indicates that broad pores do not contribute in a significant way to the surface area of S series, particularly for the 1S and 5S samples.

From the slope of the linear region of the t plots it is possible to estimate another series of surface area values: S_t. These values, which account for the surface

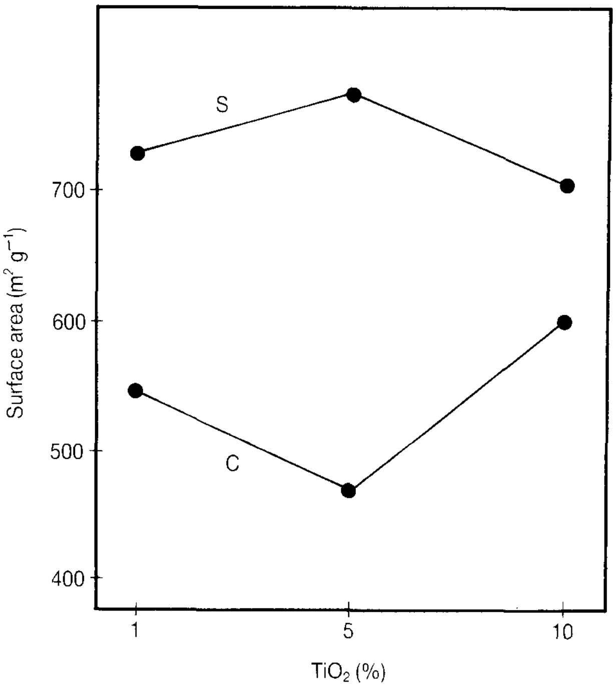

Figure 2 Effect of the TiO_2 loading and of the preparation method (C or S) on the BET surface area of the aerogels.

TABLE I Analysis of the porous structure of sono and classic gels

Sample	BET surface (m^2g^{-1})	C parameter, BET equation	t surface (m^2g^{-1})	Pore volume ($cm^3\ g^{-1}$) (1)[a]	Pore volume ($cm^3\ g^{-1}$) (2)[b]	ρ_a^{*c} ($g\ cm^{-3}$)	ρ_a^d ($g\ cm^{-3}$)
1S	727	47	642	1.15	1.22	0.62	0.64
5S	774	125	768	1.17	1.27	0.62	0.60
10S	704	84	682	1.63	1.72	0.48	0.56
1C	546	58	509	2.71	2.74	0.32	0.31
5C	465	118	459	2.70	2.75	0.32	0.31
10C	598	147	599	2.87	2.91	0.30	0.34

[a] From pore-size distribution analysis.

[b] From nitrogen uptakes at $P/P_0 = 0.995$.

[c] From pore volume drawn by pore size distribution analysis.

[d] From mercury pycnometry.

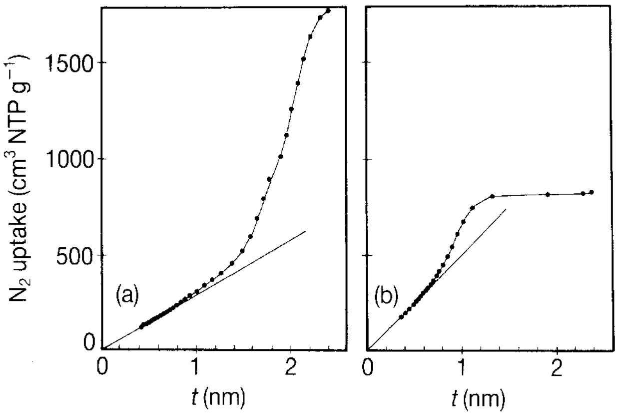

Figure 3 t plots characteristic of C and S type samples. (a) 5C, (b) 5S.

of meso and macropores, are in good agreement with those obtained by the BET method, Table I.

The IUPAC guidelines for the calculation of pore-size distributions from adsorption measurements recommend the use of the desorption branch to be avoided for those materials in which the isotherms present H2-type hysteresis loops [16]. For this reason, in our case the analysis was performed starting from the data obtained in the adsorption branches. The Pierce method was applied for the calculations [18]. Fig. 4 show the results for the case of representative S and C samples.

According to these results, the S series present a single maximum in their distributions, centred around 3.0 nm, and a strong decay for pore volumes associated to larger values of radii. This decay is sharper for the low content titania–silica sonogels (see 1S in Fig 4). However, for the C series, a much broader pore-size distribution is obtained in which pores in the range from 1.5–35 nm contribute in a significant way to the pore volume of the aerogels. Two maxima, a weak one at 2.0 nm, and a second broader and stronger one centered at about 15 nm, are characteristic of C-type samples.

Cumulative pore volume values, V_p, can be drawn from the above mentioned pore-size distributions analyses according to the Pierce method. These data are reported in Table I. If a gel can be described as a solid skeleton with voids, assuming a value for the skeletal density, ρ_s, it would be possible to estimate the apparent densities of gels, ρ_a^*, according to

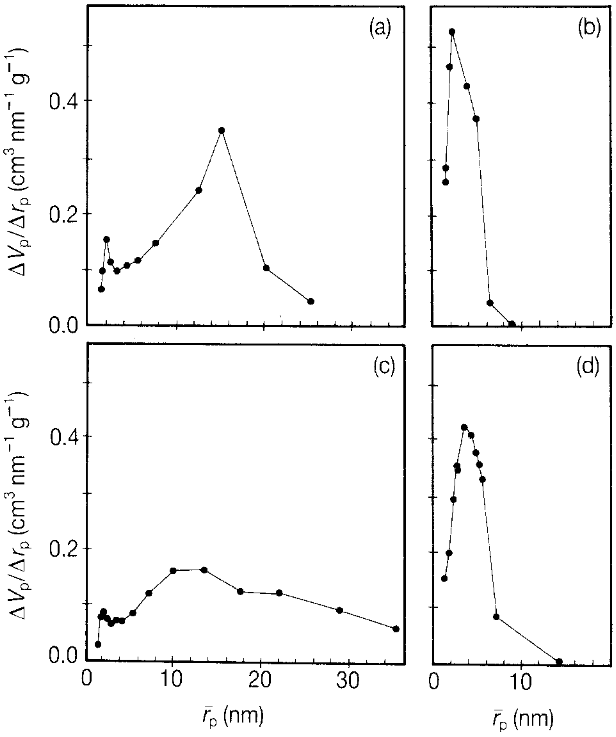

Figure 4 Pore-size distribution results of TiO_2–SiO_2 aerogels. (a) 1C, (b) 1S, (c) 5C, (d) 5S.

$$\rho_a^* = 1/\left(V_p + \frac{1}{\rho_s}\right) \qquad (1)$$

A ρ_s value of 2.2 has been used for these calculations in agreement with the results discussed elsewhere [19]. The ρ_a^* data can be compared with those obtained by mercury pycnometry, ρ_a. As can be seen in Table I, there is a fairly good agreement between both series of apparent density values. This suggests that the pore-size distribution analysis carried out in this work accounts, with a good level of approximation, for the real pore volume of the aerogels. As can be observed in Table I, sonogels are much denser than their classic counterparts.

Fig. 5 shows transmission electron micrographs representative of S and C samples, particularly for the case of 1% and 5% TiO_2 loadings. Three features of these micrographs deserve special comment. First, the

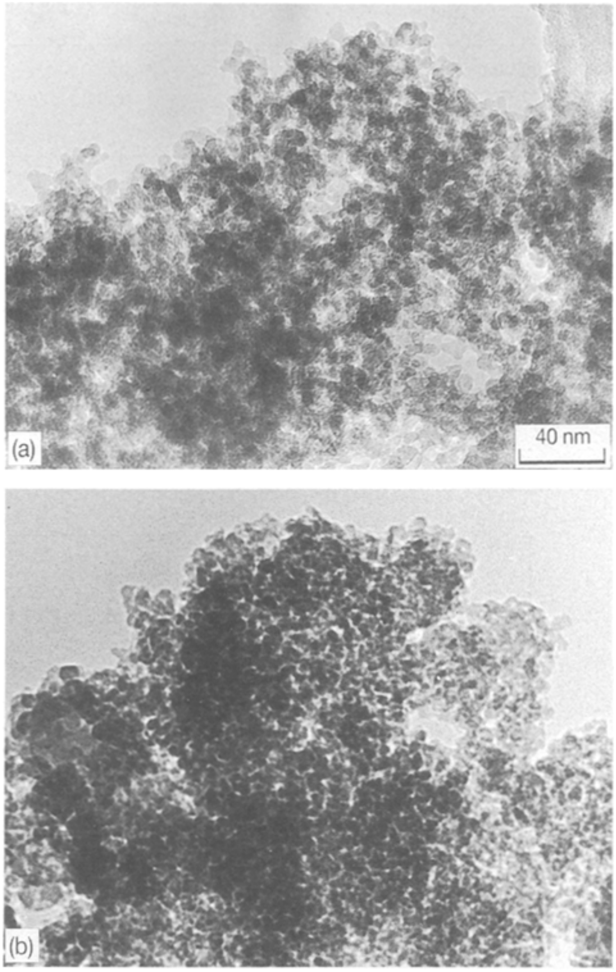

Figure 5 Transmission electron micrographs of (a) 5C and (b) 5S samples.

size distribution of the particles which constitute the gel network is neatly shifted to lower values for the S samples. Average particle sizes for 5S and 5C gels can be estimated as 5 and 8 nm, respectively. Another point is that the level of aggregation of particles is much higher for the S sample. Sample C presents a more open microstructure with a lower level of interconnection between the particles. This result is in agreement with the apparent density values shown in Table I. Finally, at the level of resolution of the micrographs it is not possible to appreciate the existence of a fractal character in either S or C samples. The elementary particles of the gel seem to be dense, and a lower scale level of aggregation into the particles is not evident from the TEM results.

4. Discussion

The first point to be noted is the occurrence of quite different textural properties for both series of gels: S and C. The sonogel route allows gels to be obtained in a shorter time, leading to materials with higher specific surface areas, higher apparent densities, smaller average particle size and finer and sharper pore-size distributions. All the samples prepared by ultrasonic activation present this series of properties if compared to their classic counterparts, although for the higher TiO_2 loading the differences in behaviour become less significant. In summary, from the point of view of the textural properties, the use of ultrasound in gel synthesis appears to be an interesting tool in order to modify the behaviour of these materials.

The values drawn for the different properties discussed in this work present a high degree of self consistency. Thus, the S_{BET} and S_t data are in good agreement suggesting that both are reliable approaches to the actual surface areas. The values of the C parameter (lower than 150) are not too high for the existence of microporosity. The absence of micropores is also confirmed by means of the t method which allowed fitting of the low-pressure adsorption uptake data by means of linear t plots crossing through the origin. The pore volumes associated to mesopores, which result from the pore-size distribution analyses, lead to ρ_a^* values similar to those directly obtained by mercury pycnometry, ρ_a; this suggests that the method used to carry out the calculations could be a reasonable choice for this type of sample, accounting for total pore volumes in good agreement with the experimental ones. The transmission electron micrographs also illustrate the different densities of S and C samples.

It is recognized that the shape of the hysteresis loop is related to the geometry of the porous structure of a material [15, 16]. Nevertheless, this is not a straightforward correlation, because pore shape and size are not the only factors determining such correlation. The type of interconnections of the porous network can also play a significant role in this problem [20, 21]. In this sense, H2 type loops, characteristic of TiO_2–SiO_2 sonogels can be considered to be the result of the existence of pores with narrow necks and wider bodies which can appear for the relatively dense S gels, although the contributions of the porous network to the hysteresis shape cannot be ruled out. The more open porous structure of C type gels would be able to explain why H1 loops are characteristic of materials prepared by the classic method. In such a case, the desorption step would be more loosely conditioned by necking effects and by interconnection of pores.

One obvious difference between C and S type gels is the possibility of obtaining gels in the absence of a solvent when gelling is carried out with ultrasonic activation. The solvent introduced in the synthesis by the classic method will be retained in the gel network, thus leading, after hypercritical drying, to specific pore volumes significantly higher than those of sonogels, whereas the TBOT precursor was introduced as a solution containing BuOH as a solvent. This fact can explain why, for the 10S sample, the density of the aerogel is shifted to lower values, thus approaching the textural behaviour of the C series.

Several other features of the sonic route deserve further comment. Ultrasound is able to produce an emulsion of alkoxide and water, thus favouring the reactivity of the mixture [1]. The foaming effect observed during the preparation of the S series can be associated with the hydrolysis reaction of the alkoxide precursor. This can be confirmed by the evolution of alcohol which is detected at such a point of the synthesis procedure. Before this moment the alkoxide–water emulsion is unstable, whereas after this point the liquid phase remains homogeneous if the irradiation with ultrasound is stopped. The alcohol formed by hydrolysis of the alkoxide can explain why the mixture is stable after this point: alcohol released during hydrolysis allows the formation of a solution. The time of irradiation after foaming is related to the gelling time [7]: the higher the irradiation time the faster the gelling process occurs. This suggests that ultrasound plays an additional role to that of allowing the formation of a stable solution.

One way in which ultrasound can favour the gelling process is by affecting the nucleation phenomena, thus controlling the final gel properties. The supply of acoustic energy can activate the formation of nuclei. As this energy is released in definite points in the reacting mixture known as hot spots [3], the chemical reactions taking place at these points can be quite different from those characteristic of a non-irradiated mixture of precursors. The transmission electron micrographs, shown in Fig. 5, suggest that the number of nuclei formed for the S sample is much higher than for the C type. This effect results in the formation of a higher number of particles, smaller in average size, for S type gels.

In a small-angle X-ray scattering (SAXS) study of the structural evolution of TiO_2–SiO_2 prepared from alkoxides by the S and C routes, it is proposed that sols constituted by filaments of polymeric-like clusters are gradually transformed with time into particles. In addition, an ageing process taking place after gel formation can also contribute to an increase in the densities of the elementary particles. No fractal character could be determined at this point of the preparation by SAXS [22]. The hypercritical drying can also modify, to some extent, the structure of the gels by favouring chemical reactions between the solvent and the wet gels [23]. In summary, the SAXS results are consistent with the apparent absence of fractal character in the micrographs shown in Fig. 5.

The results presented in this work open the possibility to design gels with precise levels of pore volume and definite pore-size distributions. The combined control of the amount of solvent and the ultrasound dose can allow the synthesis of gels with tailored textural properties. Other interesting aspects to be considered are the effects of the method of preparation on the titanium distribution into the silica matrix and on the surface chemical properties of the resulting materials. These can be relevant features from the point of view of the possible applications of these materials. For instance, the catalytic properties of these gels will be dependent on their surface chemistry, that will probably be conditioned by the method of preparation, whereas, to date no published results have been published on the effect of ultrasound on the surface chemical properties of gels. As TiO_2–SiO_2 based materials have found increasing application as catalysts [11, 12, 24] the study of these systems deserves further attention in the near future.

In conclusion, the results discussed in this paper show that the use of ultrasound can be a powerful tool in order to obtain gels with controlled textural properties.

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References

1. J. LINDLEY and T. J. MASON, *Chem. Soc. Rev.* **16** (1987) 275.
2. K. S. SUSLICK, *Mod. Syn. Meth.* **4** (1986) 1.
3. K. S. SUSLICK, D. A. HAMMERTON and R. E. CLINE, *J. Amer. Chem. Soc.* **108** (1986) 5641.
4. M. TARASEVICH, *Amer. Ceram. Soc. Bull.* **63** (1984) 500.
5. L. ESQUIVIAS and J. ZARZYCKI, in "Ultrastructure Processing of Advanced Ceramics", edited by J. D. Mackenzie and D. R. Ulrich (Wiley, New York, 1988) p. 255.
6. L. ESQUIVIAS, C. FERNÁNDEZ-LORENZO and J. M. RODRÍGUEZ-IZQUIERDO, *Rivista della Staz. Sper. Vetro* **5** (1990) 85.
7. M. RAMÍREZ del SOLAR, N. de la ROSA-FOX, L. ESQUIVIAS and J. ZARZYCKI, *J. Non-Cryst. Solids* **121** (1990) 40.
8. *Idem, ibid.* **121** (1990) 84.
9. Y. LIRONG and G. GUOXING, *J. Non-Cryst. Solids* **100** (1988) 309.
10. Z. DENG, E. BREVAL and C. PANTANO, *ibid.* **100** (1988) 364.
11. S. IMAMURA, H. TARUMOTO and S. ISHIDA, *Ind. Engng Chem. Res.* **28** (1989) 1449.
12. K. L. WALTHER, A. WOKAUN, B. E. HANDY and A. BAIKER, *J. Non-Cryst. Solids* **134** (1991) 47.
13. S. DOEUFF, M. HENRY, C. SANCHEZ and J. LIVAGE, *ibid.* **89** (1987) 206.
14. M. PRASSAS, J. PHALIPPOU and J. ZARZYCKI, *J. Mater. Sci.* **19** (1984) 1656.
15. S. J. GREGG and K. S. W. SING, in "Adsorption, Surface Area and Porosity", 2nd Edn (Academic Press, London, 1982) p. 111.
16. K. S. W. SING, D. H. EVERETT, R. A. W. HAUL, L. MOSCOU, R. A. PIEROTTI, J. ROUQUEROL and T. SIEMIENTEWSKA, *Pure Appl. Chem.* **57** (1985) 603.
17. A. W. ADAMSOM, "in Physical Chemistry of Surfaces", 4th Edn (Wiley, New York, 1982) p. 552.
18. C. PIERCE, *J. Phys. Chem.* **57** (1953) 149.
19. J. M. RUIZ-RUBE, M. RAMÍREZ del SOLAR, N. de la ROSA-FOX and L. ESQUIVIAS, in "Basic Features of the Glassy State", edited by J. Colmenero and A. Alegria (World Scientific. Singapore, 1990) p. 68.
20. V. MAYAGOITIA, in "Studies in Surface Science and Catalysis", Vol. 62, edited by F. Rodriguez-Reinoso, J. Rouquerol, K. S. W. Sing and K. K. Unger (Elsevier, Amsterdam, 1991) p. 51.
21. D. K. EFREMOV and V. B. FENELONOV *ibid.*, Vol 62, p. 115.
22. M. RAMÍREZ del SOLAR, L. ESQUIVIAS, A. F. CRAIEVICH and J. ZARZYCKI, *J. Non-Cryst. Solids*, **147** (1992) 206.
23. M. PAUTHE, J. F. QUINSON, H. HDACH, T. WOIGNER, J. PHALIPPOU and G. W. SCHERER, *ibid.* **130** (1991) 1.
24. C. U. INGEMAR ODENBRAND, S. L. T. ANDERSON, L. A. H. ANDERSON, J. G. M. BRANCHIN and G. BUSCA, *J. Catal.* **125** (1990) 541.

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