ENGINEERING OF NANOPOROUS MATERIALS USING THE SOL-GEL METHOD. EDUCATIONAL EXAMPLES

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Abstract — *Structural properties of nanoporous sol-gel materials (aerogels and xerogels) have been investigated using different characterisation techniques (transmission electron microscopy, small-angle X-ray scattering and gas adsorption) to show that they afford a coherent, consistent picture in nanometer scales from different perspectives. These studies may be used as examples in the education process to show the potentials and limitations of each of the method.*

Index Terms ¾ Aerogels, characterisation methods, sol-gel materials, xerogels.

INTRODUCTION

Porosity in nanometer scales is a crucial factor for catalysts and adsorbents and the ability to obtain highly porous solids with the specific surface area counted in hundreds of m^2/g and pore size distributions tailored to the specific needs is of prime importance. In addition, unique properties of the materials' surface are required and they can be achieved only if intimate mixing of compounds in, preferably, atomic scales is obtained.

The sol-gel method appears to be particularly attractive to achieve these objectives since the process is carried out in a liquid phase, at near ambient temperatures, with the additional positive effect on the overall energy consumption and environment. In this way both technological and social goals are achieved.

The final structure of dry material depends, however, also on the applied method of drying. If it is carried out in such a way that surface tension forces are markedly reduced, if not entirely eliminated, the structure of dry solids obtained (called aerogels) portrays that of a solid backbone of wet gel. It is very open and porosity may be as high as 99%, and surface area up to ca. 1000 m^2/g. If, however, wet gels are dried conventionally, the surface tension forces lead to a partial collapse of gel structures and the dry solids obtained, called xerogels, are less porous. Their surface area may yet be quite large, sometimes even over 1000 m^2/g. Thus, the final structure of dry gels depends on the synthetic procedure and the method of drying and hence on the aggregate of the knowledge and skills of synthetic chemists and process engineers supported by data provided by available characterisation techniques.

However, while the formation of wet gel appears to be more important, or at least it can be affected more easily, it is the surface structure (texture) of dry solids that matters and is the objective of ultimate interest and characterisation. To get a deeper insight into the complexity of internal structure of dry gels, and hence a better understanding of the mechanisms of their formation, it is desirable to probe the structure using several independent techniques. The small-angle X-ray or neutron scattering methods (SAXS, SANS), the nitrogen adsorption method and electron transmission microscopy (TEM) are most often used for this purpose.

Both SAXS and SANS have been extensively used to investigate the structure of gel backbones whereas adsorption methods are applied to investigate the properties of texture. Each of these techniques portrays the structure (or surface texture) in much the same (nanometer) length scales, yet from a different perspective. This is an important aspect since it makes it possible to obtain a fairly complete, consistent, quantitative picture of the object in nanometer scales, which is vital for the process/product control and the development of new materials.

The chemical engineers, due to their versatile education, are often positioned in a central point of the teams working on nanomaterials and play a pivot role. Therefore, we deem necessary to create in the students' minds the general 'feeling' of nanometric scales, awareness of the potentials and limitations (or even pitfalls) of the specific techniques or mathematical models used in the characterisation of nanoporous materials.

Another important issue is the ability to integrate information coming from different sources to obtain a consistent, reliable picture of the structure. In the following we present examples emerging from our research of nanoporous materials, which can be used to support the education process.

NANOPORE STRUCTURE SEEN BY SAXS AND TEM

While the examination of nanostructure using the TEM technique is very instructive and useful, the well known problem of converting 3D objects into planar images is a severe disadvantage of this method. Another characteristic feature is that observations afford the image of a selected object and not of an 'average sample'. The small-angle X-ray scattering method does not provide images of nanoporous structures as spectacular as TEM. However, in

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recent years several groups have demonstrated clearly that it may be quite useful to obtain additional, lacking information on the porous structure in the length scales range of 7-400 . Another important advantage is that the SAXS data are averaged over the whole sample investigated.

Figure 1 presents TEM images of two fairly similar fine polymeric structures of silica in aerogel samples prepared using two different catalysts [1].

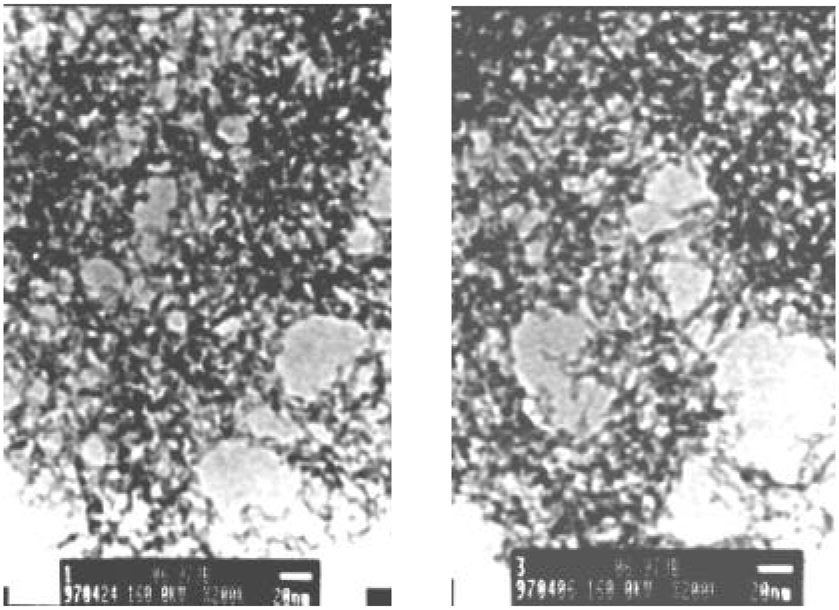

FIGURE 1.
TEM IMAGE OF AEROGELS: A0 (LEFT) AND A30 (RIGHT).

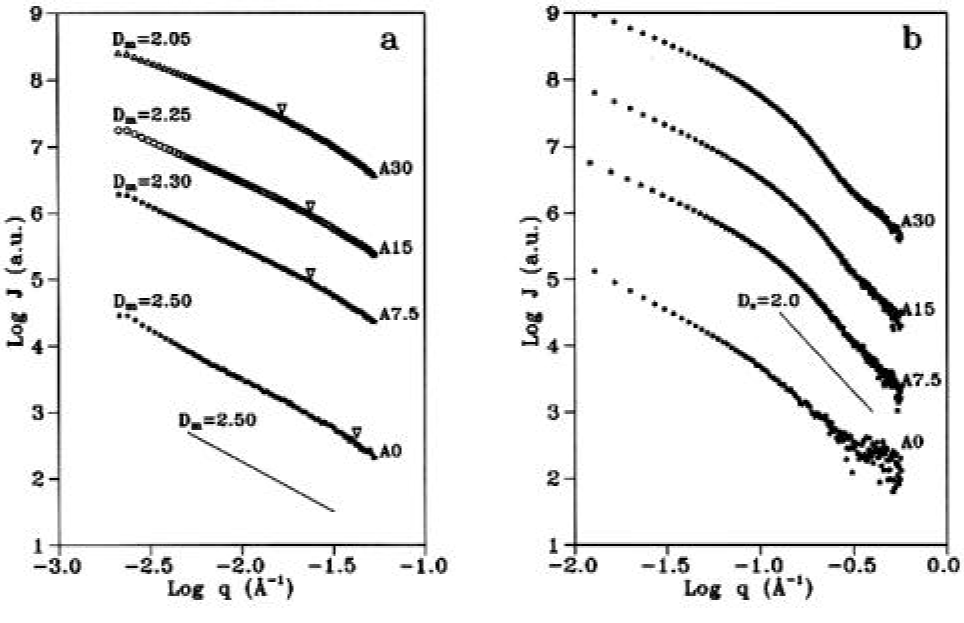

FIGURE 2.
INTENSITY AGAINST SCATTERING VECTOR FOR A0 AND A30 AEROGELS.

We can easily estimate the polymeric chains' thickness (equal ca. 4 nm) and find that both structures are very open indeed. We can also speculate that the polymeric network in one sample is perhaps somewhat sparser than the other one.

At first sight, the shapes of the corresponding intensity curves (A0 and A30 in Figure 2) plotted against scattering vector q are also fairly similar. However, the precise information regarding the structure, hidden in the shape of SAXS curves, is embedded in the slope of intensity curves plotted against vector q (reciprocal of length scales). Thus, after closer examination of two curves from this point of view a notable difference in the ramification of the polymeric structures in the length scales of tens of nm was revealed. In larger scales (small q-values) the value of mass fractal dimension, D_m in A0 sample was found equal to ca. 2.5 (as postulated by the percolation theory) whereas in A30 it was only 2.05. Moreover, application of the intermediate catalysts concentrations resulted in the consistent increase of D_m values (cf. Figure 2).

This indicates a notable potential of the SAXS method in investigations of the solid phase ramification of nanoporous structures. Obviously, the difference in the solid phase structure stems from a difference in the kinetics of gelation caused by the use of different catalysts. This example shows how precise information regarding the nanostructure can synthetic chemists gain from structural investigations. On the opposite side of intensity curve, in very short scales (large q-values) the slope from A0 curve is markedly less than that from A30. The latter value conforms to the scattering from the smooth surface (surface fractal dimension, D_s=2.0) as postulated by the Porod law $I \sim q^{-4}$ (for desmeared curves). Thus, we may conclude that the primary silica particles forming polymeric structure are in the case of A30 material quite smooth, and hence quite compact in subnanometer length scales unlike in A0 sample where they have fairly rough surface (D_s 2.5) and hence perhaps also less compact structure. Further processing of the same intensity curve can give the average size of primary particles (ca. 3 nm) and this agrees quite well with the estimates of the polymeric chains' thickness obtained from TEM images. Thus both methods give consistent results and complement each other.

As already mentioned the strategy of drying has a profound impact on the solid gel structure. This can be seen from TEM images of aerogel and xerogel of the same chemical composition displayed in Figure 3 [2]. Aerogel composite was obtained from drying in a supercritical carbon dioxide whereas xerogel sample from the conventional drying in a covered vessel under ambient conditions. As can be inferred from the corresponding SAXS curves (cf. Figure 4) the aerogel particles' surface is somewhat rough in a broad range of shorter scales (wide range of surface fractality D_s =2.4) unlike that of xerogels sample which is fairly smooth in very short scales (D_s=2.0) [3]. The latter observation stems from the collapse of small pores during drying.

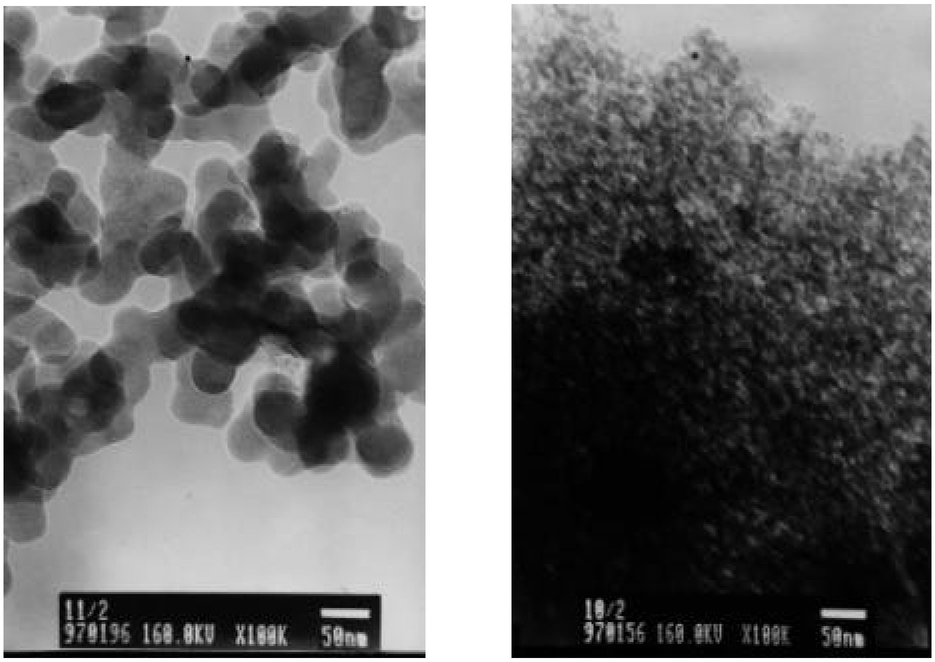

FIGURE 3.
TEM IMAGE OF AEROGEL (LEFT) AND XEROGEL (RIGHT).

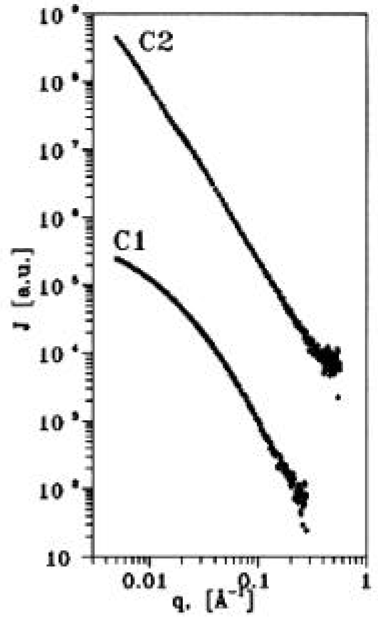

FIGURE 4.
SCATTERING CURVES FROM SiO_2-$CaCl_2$ COMPOSITES.

NANOPORE STRUCTURE SEEN BY SAXS AND GAS ADSORPTION METHOD

Nitrogen adsorption at 77 K is a standard method for texture characterization. An ample literature provides a host of mathematical/modelling tools designed to extract quantitative information regarding the specific surface structure properties, e.g. pore size distribution (PSD) or specific surface area, from the experimental adsorption isotherms. While, intuitively we can expect a fairly good agreement between the structure portrayals by TEM and the texture characteristics obtained from adsorption experiments the question regarding the level of consistency between information extracted from SAXS and nitrogen adsorption method seems to be well posed and deserving consideration.

Figure 5 presents pore size distribution (obtained using a standard BJH method) in aerogel and xerogel samples previously analysed by TEM and SAXS (Figures 3 and 4). In aerogel we see a very broad and diffused PSD covering the whole range of mesopores (2-50 nm diameter according to IUPAC) and small macropores (>50 nm) whereas in xerogel this peak is quite narrow and pronounced and corresponds to pores 6-10 nm in diameter. The corresponding intensity curves from both samples are also notably different, as discussed before (cf. Figure 4). The slope of the scattering curve from xerogel sample corresponds, in the uppermost q-region ($q > 0.03\ ^{-1}$), to D_s=2.0 and hence smooth surface (i.e. devoid of pores of the appropriate size) whereas in the larger scales (smaller q's) this slope gradually decrease with q, which signifies non-polymeric and non-fractal rough surface structure. For $q<0.01\ ^{-1}$ the scattering curve levels out which signifies a uniform structure in the larger scales (implying a lack of larger pores/objects). Note that this perfectly agrees with the PDS detected by the nitrogen adsorption method. Also noteworthy is a perfect agreement between an extensive surface fractality quantified by D_s=2.4 (moderate surface roughness) seen in C2 sample and a diffused PSD revealed by the nitrogen adsorption method.

A similar good agreement of SAXS and PSD characteristics could also be observed in the aerogels displayed in Figures 1 and 2 (cf. Figure 6). In A0 aerogel we can observe a considerable presence of very small pores whereas in A30 it is far less, and this is in concert with the fractal surface characteristics extracted from SAXS curves. In the larger scales the opposite feature of PSD is observed and this again conforms to the mass fractal picture of the structure, less ramified (and hence sparser) in A30 than in A0.

The consistency of observations between SAXS and nitrogen adsorption method has been confirmed also in investigations of another nanoporous materials [4]. On the whole good quantitative agreement between surface structure portrayals extracted from SAXS curves (using fractality concepts) and porous texture portrayals has been obtained.

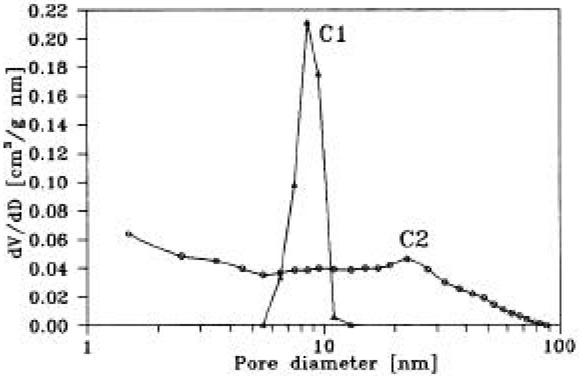

FIGURE 5.
PORE SIZE DISTRIBUTIONS IN SiO_2-$CaCl_2$ COMPOSITES.

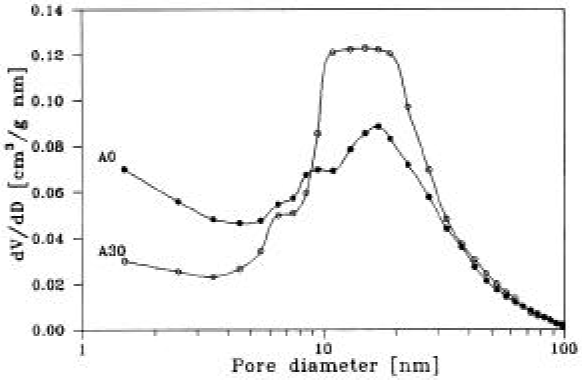

FIGURE 6.
PORE SIZE DISTRIBUTIONS IN AEROGELS A0 AND A30.

CONCLUDING REMARKS

The examples presented above clearly demonstrate great potentials of the available characterisation techniques, the significance of an appropriate interpretation of data and the abundance of information contained. Students should be made aware of this during the course of studies. Another, equally important aspect, is the understanding and interest for working together to achieve the mutual goal. This is what we deem most crucial for all people in the XXI century and what we teach students in our university.

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