

## Bimodal Mesopore Distribution in a Silica prepared by Calcining a Wet Surfactant-containing Silicate Gel

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Calcination of a wet surfactant silicate gel results in a bimodal mesopore system in which the smaller pores are distributed at around 30 Å and the larger range from 80 to 200 Å in diameter.

A new family of mesoporous silicas or silicates (designated M41S) with well-defined pore sizes have been synthesised<sup>1-5</sup> from aqueous silicate gels containing surfactant molecules as a templating agent, and among the members of the family is the MCM-41 which possess a hexagonal array of mesopores. Depending on the synthetic conditions, the pore diameters of these materials vary within the range 20 to 150 Å. However, the successful synthesis of mesoporous silicas with a pore diameter larger than 50 Å has to be conducted, to our knowledge, in the presence of auxiliary molecules such as mesitylene as a filler in the reaction mixture. Furthermore, no double-mesopore silicas or silicates prepared *via* a surfactant-gel route have appeared in the literature. In this communication, we describe an unusual silica formed by calcination of a wet surfactant-containing silicate gel; the material possesses a bimodal mesopore distribution with the well-defined smaller pores being distributed at around 30 Å in diameter and the larger within the range 80–200 Å. No filler molecules were used in the preparation of this silica material.

The formation of the double-mesopore silica relies on the calcination of a wet gel precursor which is prepared by mixing tetraethylorthosilicate, sodium hydroxide and a surfactant in an aqueous medium at room temperature. Thus, NaOH was dissolved in distilled water and mixed with the surfactant cetyltrimethylammonium chloride (CTACl). The mixture was stirred until homogeneous followed by dropwise addition of tetraethylorthosilicate. A thick gel formed from the final mixture after further stirring for about 4 h. The typical gel composition was CTACl:0.14Na<sub>2</sub>O:5.1SiO<sub>2</sub>:360H<sub>2</sub>O without accounting for the ethanol evolved from the silicon source. The wet gel precursor was then subjected to calcination in air at 550 °C.

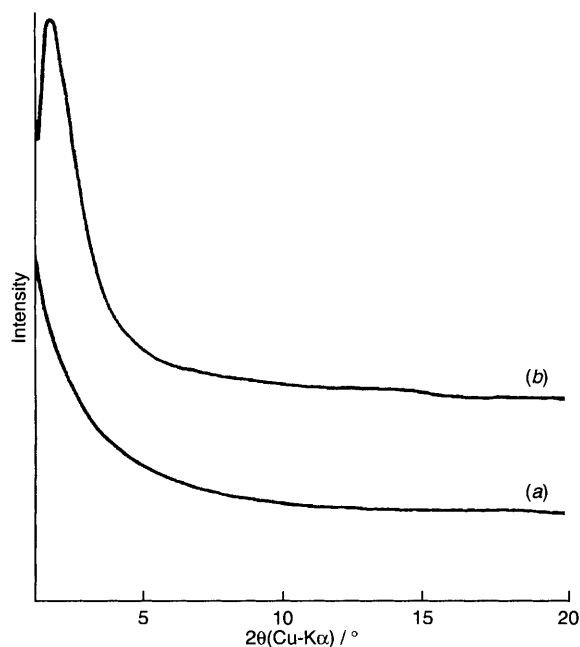


Fig. 1 X-Ray powder diffraction patterns of (a) the surfactant-containing gel dried at room temperature and (b) the sample formed by calcination of the wet gel at 550 °C

Fig. 1 shows the XRD pattern of the gel precursor dried at room temperature and that of the sample calcined at 550 °C for about 1 h. It is seen that the gel at room temperature is highly amorphous since there is no diffraction peak on its XRD pattern whereas the sample calcined at 550 °C exhibits some crystallinity as suggested by the diffraction peak at around 1.7° (Cu-Kα 2θ), corresponding to a *d*-spacing of 50 Å. Assuming that the peak arises from the (100) reflection of a hexagonal array of mesopores, as is the case for the mesoporous MCM-41, the diameter of the pores must be less than 50 Å. The appearance of the (100) reflection on the XRD pattern for the calcined sample suggests that during calcination a hexagonal array of well-defined mesopores is formed. It is probable that in the gel precursor, which is completely XRD-amorphous, silica mesopores filled with templating molecules already exist but in a disordered way. Calcination removes the templating molecules from the pores and renders the latter orderly arrayed.

The N<sub>2</sub>-adsorption-desorption isotherm and the pore size distribution obtained on an ASAP 2400 automatic adsorption instrument for the calcined silica are shown in Fig. 2. It is obvious from the hysteresis loop of the isotherm<sup>6,7</sup> that mesopores are indeed present in the material. Nevertheless, the pore size distribution based on the desorption branch reveals that there are two mesopore sizes in the material, *i.e.* a bimodal distribution: one with an average pore diameter of about 30 Å

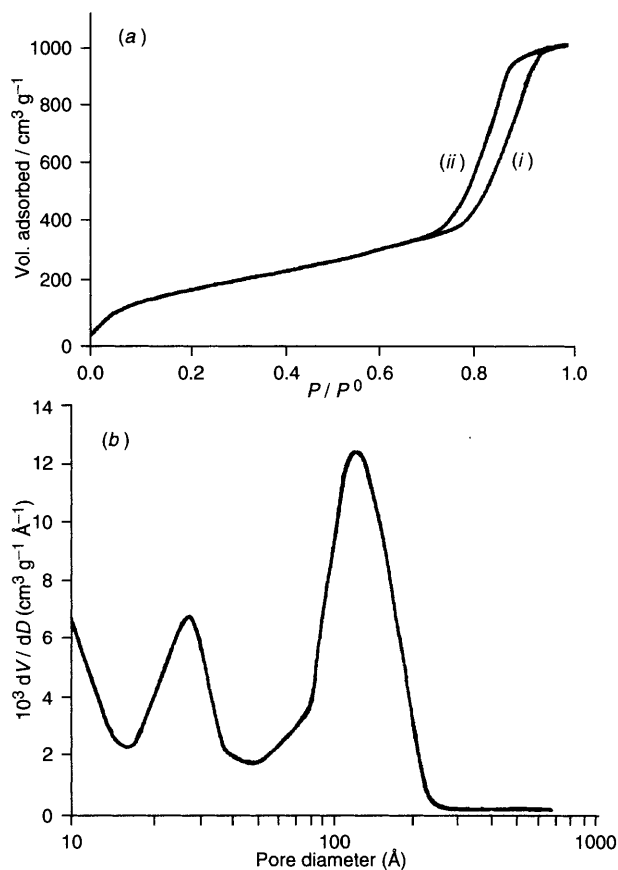


Fig. 2 (a) N<sub>2</sub>-adsorption (i)-desorption (ii) isotherm on the calcined sample at STP and (b) the pore size distribution of the material

and the other distributed within the range 80–200 Å. It is likely that the former corresponds to the XRD reflection with a  $d$ -spacing of 50 Å. In this case, the thickness of the walls around these pores is about 20 Å, larger than that (*ca.* 10 Å) of the mesoporous MCM-41 synthesised hydrothermally.<sup>1–4</sup> The majority of the mesopores, however, are those with diameters within the range between 80 and 200 Å [the maximum of the distribution curve (Fig. 2) is at around 110 Å]. It is believed that these large mesopores are similar to those present in amorphous mesoporous silica gels, being formed by the packing of small silica particles.<sup>8</sup> Differing from normal amorphous porous silica gels, the particles in the present silica material contain well-defined small mesopores which are responsible for the XRD reflection at 1.7°. The total pore volume for the narrow pores (30 Å) is only 0.12 cm<sup>3</sup> g<sup>-1</sup>, corresponding to a total surface area of 150 m<sup>2</sup> g<sup>-1</sup>, whereas that for the large pores (110 Å) is 1.35 cm<sup>3</sup> g<sup>-1</sup> with a total surface area of 430 m<sup>2</sup> g<sup>-1</sup>. The small pore volume for the narrow pores explains that an inflection at around  $P/P^0 = 0.35$  according to the Kelvin equation<sup>6,8</sup> is not discernable on the adsorption–desorption isotherm.

The Na<sub>2</sub>O:SiO<sub>2</sub> ratio in the gel affects to a great extent the appearance of the XRD patterns of the precursor and the calcined samples. For instance, when all the other ratios remain unchanged, Na<sub>2</sub>O/SiO<sub>2</sub> > 0.25 leads to a gel precursor, the XRD pattern of which clearly shows a peak between 1 and 2°, whereas when Na<sub>2</sub>O/SiO<sub>2</sub> is < 0.12, no diffraction peak

appears at all, even on the XRD patterns of the samples treated at elevated temperatures.

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