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Control of pore size distribution of silica gel through sol–gel process using water soluble polymers as additives

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To control the pore size distribution of silica gel, several kinds of water soluble polymers were added in the sol–gel process starting from tetraethyl orthosilicate. The polymers employed here were classified into three groups. The first group comprised uncharged polymers such as polyvinyl alcohol and polyethylene glycol, which affected only the amount of micropores and small mesopores (<20 nm). The second group comprised charged polymers (polyelectrolyte) such as polyacrylic acid (anionic) and a quaternary salt of polyethylene imine (cationic), which significantly increased the number of larger mesopores (>20 nm). The third group comprised proteins such as lipase and albumin and decreased the number of micropore and mesopores and greatly increased the number of macropores. The results could almost be explained in terms of the principal effects of the polymers on a process of sol particle growth.

1. Introduction

Much attention has been paid recently to the preparation of a metal oxide by the sol–gel process starting from the metal alkoxide [1–3]. The sol–gel process consists of the formation of sol particles through the hydrolysis of the metal alkoxide and polycondensation of the hydrolysate, the gelation of sol particles and then the drying of the hydrogel, followed by calcination or sintering of the dry gel. It has the advantage that glasses [4–6], fibres [7–9] and coating films [10, 11] can easily be produced. It is also favourable for providing pure metal oxide because the metal alkoxide, which has properties similar to those of organic compounds, is used as a raw material.

Incidentally, silica is one of the typical metal oxides which have been used as supports of solid catalysts. In recent years it has also been applied as a support of immobilized enzymes. For solid catalytic reactions, reaction properties have been noted to be dependent not only on catalyst properties but also on pore structures of the supports. In the catalytic reactions accompanying coke formation, the cokes deposit on the surface of catalysts and, therefore, reduce their catalytic activity. For catalysts for which pore size distribution is suitably designed, however, the catalytic fouling is known to be less [12]. In coal liquefaction it has been shown that a catalyst properly having both mesopores and macropores exhibits higher catalytic activity because of their fitness for the penetration of large molecules relating to the reaction [13]. In the case of an immobilized enzyme, only macropores, in which the enzyme can be trapped, may be effective. It is, thus, important for such reactions to control the pore size distribution so that supports may have relatively large pores from the meso to the macro range.

In this work, for the control of pore size of silica gel, we prepared the gels via the sol–gel process modified with the addition of water soluble polymers. The pore size distributions were discussed in connection with the properties of the added polymers.

2. Experimental procedure

Fig. 1 shows the procedure for preparing the silica gels. Tetraethyl orthosilicate (TEOS) of 5 g, 30 g deionized water and a desired amount of a water soluble polymer (up to 37.5 wt %) were mixed and then the hydrolysis started with the addition of HCl. The reaction was continued for 1.5 h at room temperature under vigorous stirring. The pH of the solution was adjusted to 1.8. After the completion of the hydrolysis, the pH of the solution was increased to 8.2 by addition of NH_4OH under slow stirring and gelation occurred. The time required for the gelation was dependent on the type and amount of the polymer added. The hydrogels were dried at 40° C for 50 h and then calcined to remove the polymer. The polymers used here were: polyvinylalcohol (PVA), Mw (weight average molecular weight) = 22 000 and 88 000; polyethylene glycol (PEG), Mw = 1000, 3000, 8500 and 50 000; polyacrylic acid (PAA); poly (p-styrenesulphonic acid sodium salt) (PSSNa); the quartarnary salt of polyethylene imine (PEI), synthesized by the reaction of PEI with HCl; lipase; albumin from egg. All of the polymers except for PSSNa were purchased from Wako Pure Chemical Ltd. They were reagent grade and were used without further purification. PSSNa was synthesized from a p-styrenesulphonic acid sodium salt by radical polymerization using

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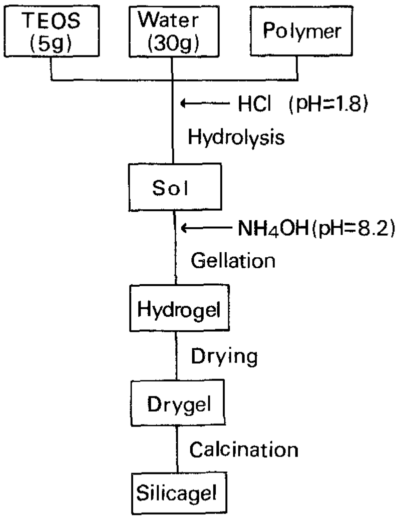

Figure 1 Preparation procedure of silica gel.

potassium peroxodisulphate as a thermal initiator. The crude polymer was purified by ultrafiltration.

The distribution of pore size of up to 30 nm diameter of micropores and mesopores was determined from a nitrogen isotherm. The isotherms were measured with BET apparatus (Sibata P-600); the distribution dV/dP as a function of P (V, pore volume; P, pore diameter) was calculated by the method developed in our laboratory [14]. Macropores with diameters above 100 nm were observed directly by scanning electron microscope (SEM, JEOL Ltd, T 330). The amount of additive was defined as a weight ratio to the TEOS.

3. Results

3.1. Pore size distributions of the gels prepared without polymer addition

Generally, in sol–gel processes, alcohol–water mixtures are used as solvents to make homogeneous TEOS solutions. In this study, however, water alone was used as a solvent so as to dissolve the polymers employed. TEOS was not initially miscible with water and dispersed like oil droplets. As the hydrolysis progressed, the solution became homogeneous. The water soluble polymers were utilized, because of the expectation for their properties such as having charge or a kind of charge, which could not be expected from hydrophobic polymers.

Prior to the polymer addition experiments, we sought the conditions for the weight ratio of TEOS to water, and pHs at the hydrolysis and gelation so that reproducible and properly hard gels might be obtained. As a result, the gels were found to have the desired hardness with satisfactory reproducibility when the weight ratio was 1/6 and pHs were adjusted to 1.8 at the hydrolysis and 8.2 at the gelation. Fig. 2 shows the effect of calcination temperature on the pore size distribution of gels which were calcined for 1 h at temperatures from 500 to 800° C. The gels were transparent and had mesopores with diameters ranging up to 10 nm. Although the pore size distribution varied at mesopores smaller than 5 nm and its variation resulted in a decrease in the surface area from about 700 to 500 $\mathrm{m^2\,g^{-1}}$ as the temperature increased from 500 to 700° C. Since those pores were less noteworthy in this work, the increase in calcination temperature can be taken as having no marked affect on the pore size distribution, therefore, the subsequent gels were calcined at 800° C for 1 h so that the polymers added might not be left in the gels. Since PSSNa, however, was hard to burn out from dry gels even under the above conditions, calcination was continued for several hours. Fig. 3 shows a SEM image of the calcined gel prepared without any additive. The surface of the gels appeared to be flat and macropores were not observed.

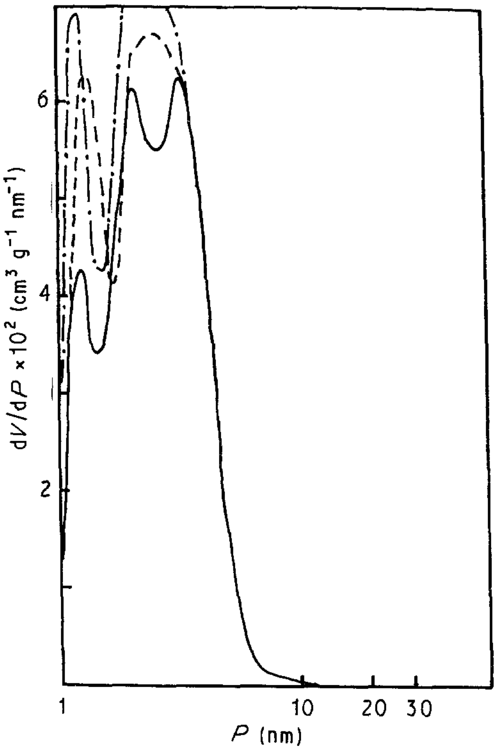

Figure 2 Pore size distribution of the gels prepared without additive. Calcination temperature: (—·—) 500° C; (– – – –) 600° C; (———) 800° C.

3.2. Effects of uncharged polymers

The gels were prepared with the addition of PVA and PEG at a constant weight addition of the polymers while their mean molecular weights were varied. All of them were transparent as were the gels prepared without polymer addition. Their surface area tends to decrease with polymer addition, as compared with that of the gel produced without the polymers.

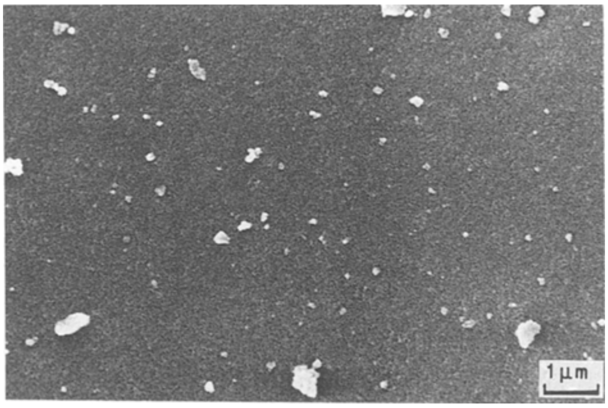

Figure 3 SEM image of the gel prepared without additive. The gel was calcined at 800° C for 1 h.

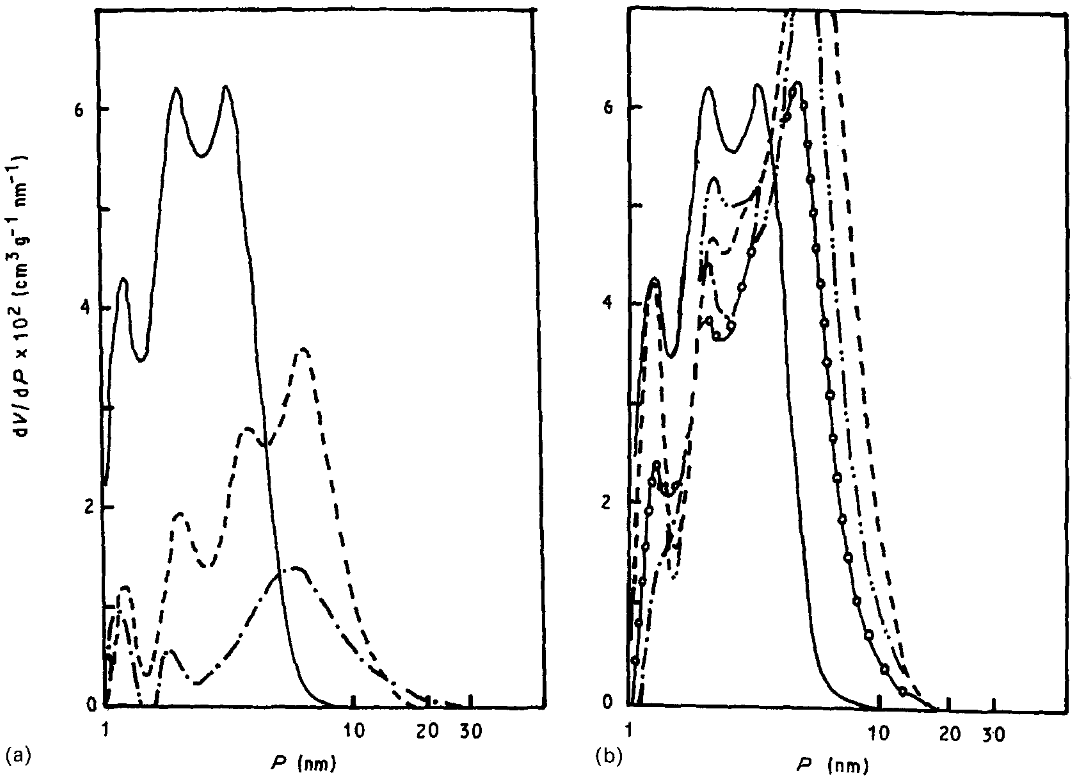

Figure 4 Pore size distribution of the gels prepared with (a) PVA and (b) PEG as additives. The amount of the polymers in starting solutions are 37.5 wt %. The molecular weight (Mw) of the additives are (a): (——) none; (– – – –) 22 000; (—·—) 88 000 and (b): (——) none; (– – – –) 1000; (—·—) 3000; (—··—) 8500; (—o—) 50 000.

Fig. 4 shows the pore size distributions of the gels. It is found that for all polymers mean pore sizes shift from 3 to 7 nm with polymer addition. Fig. 5 shows a SEM image of the gel obtained with PVA. From the micrograph, their surface appeared to be flat and macropores were not observed. The PEG addition gave SEM images similar to those for the PVA addition.

3.3. Effects of polyelectrolytes

A silica particle has an isoelectric point at pH from 1.4 to 3.0. Above the values, its surface has a negative electric charge and otherwise it has the opposite charge, therefore, it was expected that the addition of electrolytes including polyelectrolytes might affect the sol particle growth and/or gelation process.

Fig. 6 shows the pore size distributions of gels prepared with the addition of PAA and PSSNa as anionic polymers. For any polymer, the distributions were significantly different from those of the gels prepared both without polymers and with the uncharged polymers. The distributions indicate that the gels formed have pores larger than 20 nm, which were not observed in the gels stated above. The number of those pores increases and that of the rest of the pores (< 20 nm) decreases with the increase of the addition. Further, they suggest that pores larger than 30 nm, which are not able to be estimated by the present method, were newly formed. As shown in Fig. 6, the number of pores of the gels for PSSNa addition is less than that for the PAA addition. This may partly be responsible for the sintering due to the more severe calcination conditions applied to the gels for PSSNa addition.

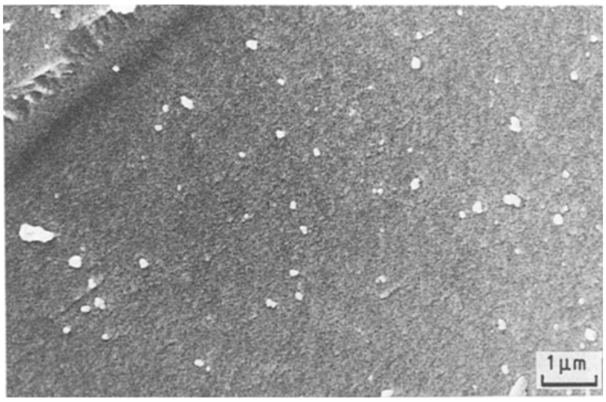

Figure 5 SEM image of the gel prepared with PVA as an additive. The amount of PVA in starting solution is 37.5 wt %.

Fig. 7 shows the pore size distribution for the addition of PEI as a cationic polymer. The distributions exhibit addition effects almost the same as those of the anionic polymers.

Although the gels prepared using the polyelectrolytes were translucent, they absorbed water slowly and became transparent. This property implies the presence of significantly sized pores. Fig. 8 shows SEM images of the gels obtained with PAA and PEI as additives. The gels are found to have fine structures, in agreement with the property suggested above.

As described previously, the kind of charge of the polymers should be expected to affect the gel structure but the experimental results did not meet this expectation, thus, only the ionic strength of the solution was suspected to affect the gel structure. To test the suspicion, low molecular weight electrolytes (NH_4Cl and $(C_2H_5)_3$ HNCl) were added. Although the mean pore size was slightly increased by the addition, significant

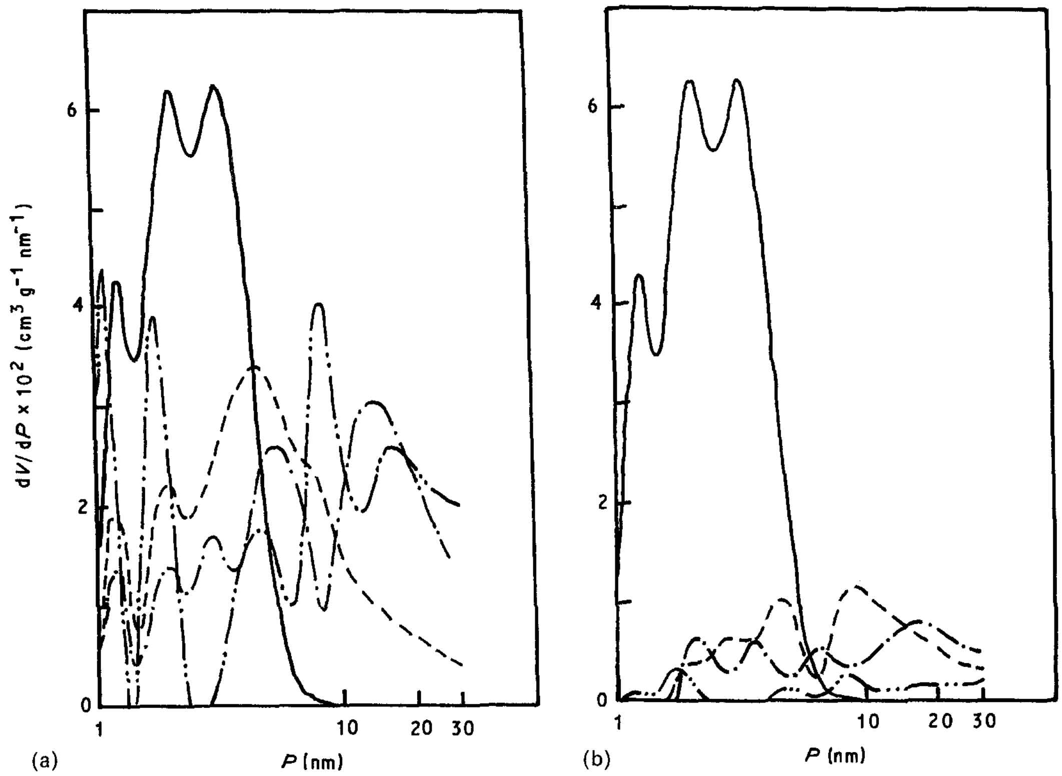

Figure 6 Pore size distribution of the gels prepared with (a) PAA and (b) PSSNa as additives. The amount of the polymers in starting solutions are (a): (———) none; (- - - -) 16.7 wt %; (—·—) 28.6 wt %; (—··—) 37.5 wt % and (b): (———) none; (- - - -) 9.1 wt %; (—·—) 16.7 wt %; (—··—) 37.5 wt %.

changes in the pore size distribution, as seen with the polyelectrolytes, were not found.

3.4. Affects of protein

Proteins have molecular structures different from those of the synthesized polymers. Most of them have globular structures, but the structures are not tight and changed to a linear or entangled form depending on the conditions of pH, temperature or the presence of denaturants, etc. It is thus interesting to know how they affect the gel structure. In this work, two commercially available proteins (lipase and albumin from egg) were used.

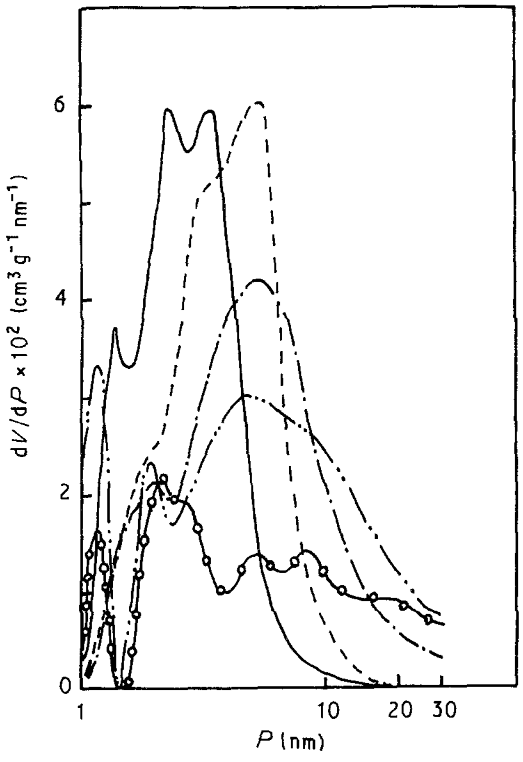

Figure 7 Pore size distribution of the gels prepared with the quaternary salt of PEI as an additive. The amount of the additive in starting solutions are (———) none; (- - - -) 0.4 wt %; (—·—) 1.0 wt %; (—··—) 2.0 wt %; (—○—) 16.7 wt %.

Fig. 9a shows the pore size distribution of the gel prepared with lipase as an additive. A significant decrease in mesopores was found by the addition. When 0.19 weight ratio of lipase was added, almost all of the mesopores diminished. The appearance of the gels resembled that of synthesized zeolite. They were fragile, as compared with the gels prepared with addition of the other kinds of polymers, and absorbed water quickly. These results imply a highly porous structure of the gels, although there were few mesopores.

Fig. 10a shows a SEM image of the gel prepared with lipase. Considerable sized macropores (~ 1000 nm) were observed in the gel and similar large macropores were found when albumin was used (Fig. 10b). Interestingly, however, the gels themselves proved to be almost non-porous owing to few mesopores.

4. Discussion

When the mechanism developed for a conventional sol–gel method is applied, the pores in the calcined gels must be made by the following sequence. The hydrogel, prepared by an acid catalyzed hydrolysis of silicate and then a base catalyzed gelation of the hydrolysate, possesses voids in its matrix which are filled with water molecules. Drying of the gel results in the shrinkage of the voids accompanied by removal of the water. The voids are finally left as pores after the

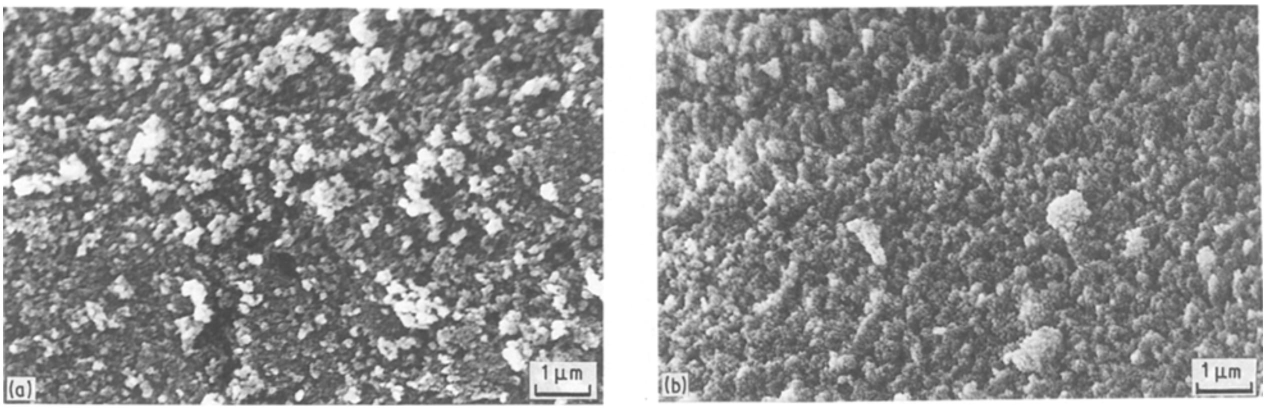

Figure 8 SEM image of the gels prepared with (a) PAA and (b) the quarternary salt of PEI as additives. The amount of the additives in starting solutions are (a) 37.5 and (b) 28.6 wt %.

calcination of the dry gels while the matrix slightly shrinks and becomes firm.

The size of the pores must depend on which step is affected by the polymer added. The effects which may be mentioned for the addition of the water soluble polymers are as follows: (1) the first one on the growth of sol particles which make up the gel matrix, i.e. their dimensions determine pore sizes; (2) the second one contributed from the volumes of the water polymers trapped in the voids, i.e. the polymers' excluding volumes determine pore sizes; (3) the third ones responsible for polymer association during the gelation and for aggregation after the drying (the polymers occur as clusters in the dry gel matrix), if the second one dominates.

The addition of the uncharged polymers brought the following experimental results. The sol solutions, and the hydro, dry and calcined gels were transparent. In the calcined gels no mesopores with relatively large diameters above 20 nm and no macropores were found while mesopores with diameter around 7 nm, which were few without addition of the polymer, were observed. Therefore, at least the pore formation was not attributed to the third effect and thus the polymers were considered to be miscible with silica and to be dispersed uniformly in the hydro and dry gels. Since the SEM images did not show any fine structures in the gels, the size of the sol particles was likely to be as small as that of the gels prepared without the addition of the polymers. Consequently, the first and/or second effects may be regarded as contributing these results though there is not enough evidence to decide which effects of them are definite.

In the case of the polyelectrolyte addition the experimental findings are summarized below. As a greater amount of polymers were added, larger mesopores were formed and their diameters exceeded 30 nm while smaller mesopores diminished. From the SEM images

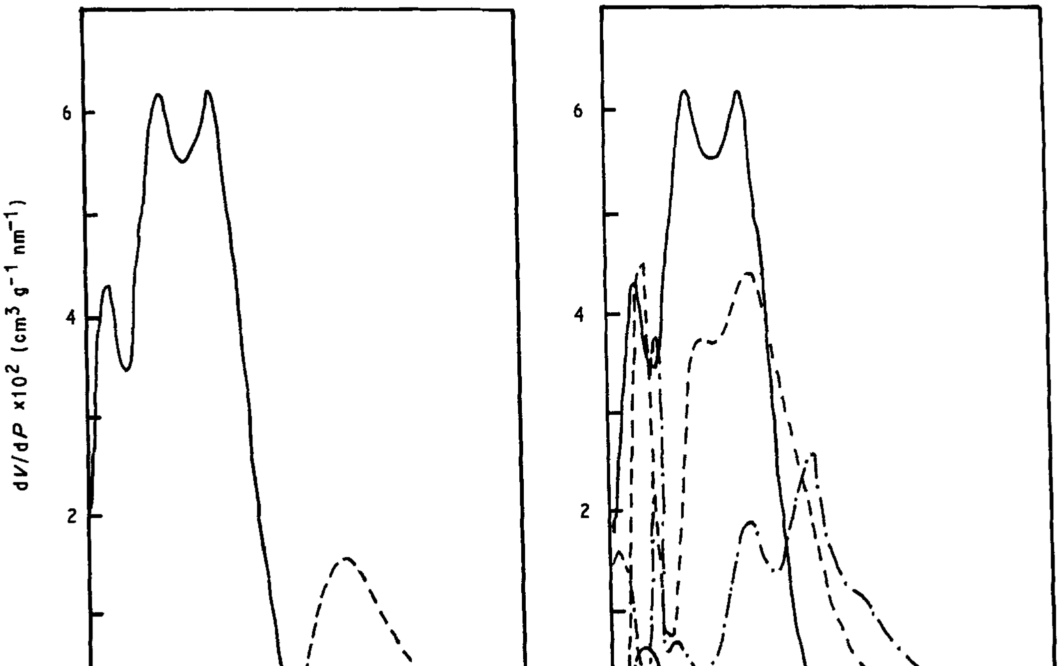

Figure 9 Pore size distribution of the gels prepared with (a) lipase and (b) albumin as additives. The amount of the additives in starting solutions are (a): (——) none; (- - - -) 2.0 wt %; (—·—) 9.1 wt %; (—··—) 16.7 wt % and (b): (——) none; (- - - -) 2.0 wt %; (—·—) 9.1 wt %; (—··—) 16.7 wt %.

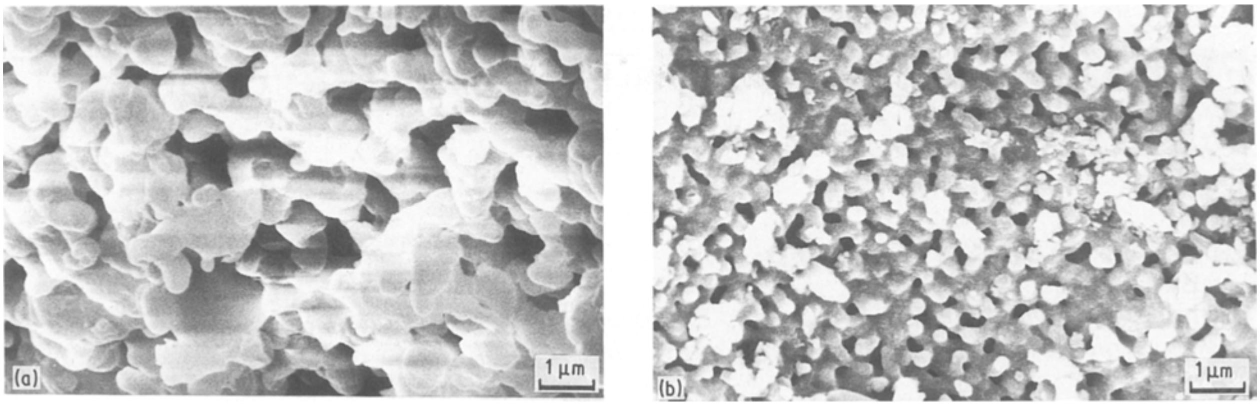

Figure 10 SEM image of the gel prepared with (a) lipase and (b) albumin as additives. The amount of both additives in the starting solution is 16.7 wt %.

fine structures made of an assembly of fine particles were observed. The first effect, therefore, resulted in those gel properties.

When the proteins were applied, calcined gels significantly different from those obtained without polymer addition were obtained. They were opaque, fragile and white, resembled synthesized zeolite and absorbed water. The number of mesopores decreased considerably with an increase of protein addition and at the 0.19 weight ratio of addition of the proteins the gels almost lost the mesopores instead of having macropores of diameters extending to several thousands of nanometres. The first effect give rise to such gels though the third one can also give these results, because the mesopores were not found which would have had to be formed if the third one had played a role. The macropores were thus spaces among sol particles far larger than those formed with no addition of the polymers. The protein solutions may be favourable to the growth of silica sol particles.

In Fig. 11, the influences of the water soluble polymers on the gel structures are schematically summarized.

4. Conclusion

Pore structures of the silica gels, prepared by the sol–gel method with addition of several kinds of water soluble polymers, were studied. Uncharged polymers affected only the formation of mesopores. These polymers were miscible with the silica hydrogel and had little influence on silica sol particle growth. Polyelectrolytes, both anionic and cationic, caused an increase in the mesopore size above 20 nm and fine structures were found in the gels by SEM measurements. The effects were explained in terms of the electrostatic interaction between the silica sol particles and the polyions. When proteins were added, mesopores were diminished significantly and large macropores appeared. The changes in the pore size distribution with the addition of the polyelectrolytes and the proteins were accounted for by their effects on the growth of silica sol particles.

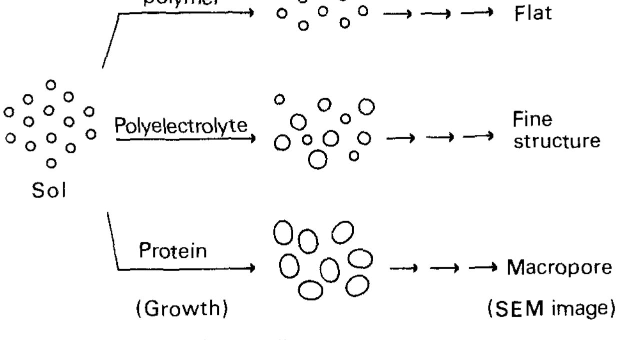

Figure 11 Influence of the additives on silica gel structure.

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