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Control of pore size distribution of silica gel through sol–gel process using inorganic salts and surfactants as additives

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For control of the pore size distribution of silica gel, the gel was prepared using the sol–gel process modified by adding several kinds of inorganic salts and surfactants. The addition of any inorganic salt decreased the gel surface area and depressed the formation of mesopores. The surface area and the volume occupied by mesopores changed with the valency of the cation of the salt used. When surfactants were employed as additives, the surface area and the pore size distribution were greatly dependent on the kind of head group of the surfactant: non-ionic surfactant addition monotonously increased the surface area owing to the formation of larger mesopores; anionic surfactant addition significantly decreased the surface area because of the decrease in the volume of mesopores; cationic surfactants caused the surface area to decrease with small additions as anionic surfactants did, while further addition raised the surface area. The rise in the surface area was due to a marked formation of smaller mesopores. These results are discussed on the basis of the interfacial properties of the additives.

1. Introduction

In catalytic reactions, catalyst activity, lifetime and/or reaction selectivity are dependent not only upon the nature of the catalyst but also upon the pore structure of the catalyst support. Thus, many workers have studied the control of the pore size distribution of catalyst supports and have proposed several methods [1–4].

Recently, the preparation of metal oxides by the sol–gel process starting from metal alkoxides has attracted much attention [5–7]. The sol–gel process consists of the formation of sol particles of a desired metal oxide through the hydrolysis of an alkoxide of the metal and polycondensation of the hydrolysate, and then the gelation of the sol particles. The process facilitates production of glasses [8–10], fibres [11–13] and coating films [14, 15] of various metal oxides. Another advantage is the ability to produce easily a variety of porous metal oxides [16]. Thus, the process can be expected to apply to the preparation of catalysts or catalyst supports. However, a conventional sol–gel process brings only mesopores with diameters below 10 nm, which are not always effective for some catalytic reactions. Some modifications are therefore, needed for the sol–gel process, allowing the gel to have a pore size distribution suitable for such catalytic reactions. In our previous study, a modified sol–gel process with the addition of several kinds of water-soluble polymer was found to be useful for the formation of large mesopores and macropores in silica gel [17].

In this work, for controlling the pore size distribution of silica gel a conventional sol–gel process was modified by the addition of inorganic salts and surfactants, and the effects of the additives on the properties of the prepared gel are discussed on the basis of their interfacial properties.

2. Experimental procedure

Fig. 1 shows the procedure for the preparation of silica gel. 5 g tetra-orthosilicate (TEOS), 30 g deionized water and a desired amount of additive (inorganic salt or surfactant), if necessary, were mixed, and then hydrolysis was started by the addition of HCl to keep the pH of the solution at 2. It took 1.5 h for completion of the hydrolysis at room temperature under vigorous stirring. After that, for gelation the pH of the solution was increased to 8 by addition of NH_4OH under mild stirring. The hydrogels obtained were dried at 40 °C for 120 h and then calcined at 800 °C for 1 h. When inorganic salts were used as additives, the calcined gels were washed with deionized water for removal of salts and were dried again.

The distribution of pore size up to 30 nm diameter was determined from N_2 adsorption isotherms; the isotherms were measured with a BET apparatus (Shibata P-600) and the distribution dV/dP as a function of P (V, pore volume; P, pore diameter) was calculated by the method developed in our laboratory [18]. Macropores with diameters above 100 nm were measured by scanning electron microscopy (SEM,

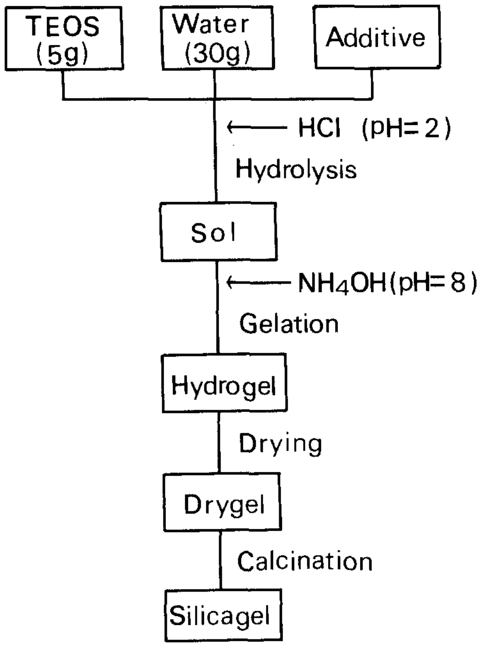

Figure 1 Preparation procedure of silica gel.

Jeol T-330). The gel structure was analysed with an X-ray diffractometer (Rigaku Denki RAD-γA).

3. Results

3.1. Pore size distribution of gels prepared by conventional process (without additive)

Fig. 2 shows the results. The pore size was distributed only from 1 to 10 nm and the specific surface was 600 to 700 $m^2 g^{-1}$. Fig. 3 shows an SEM image of the gel. The surface was flat and no macropores were found. Therefore, although the method was able to give a surface area sufficient for a solid catalyst, it needed some modification so as to develop larger pores.

3.2. Pore size distribution of gels prepared by modified process

3.2.1. Inorganic salt addition

Since some ionic species are supposed to participate in the sol–gel reaction, the addition of inorganic salts must affect sol particle growth and the gel structure. Their effects are considered to be due to compression of the electric double layer around the ionic species to alter the pore size distribution of the gel. The effects are expected to depend mainly on the kind of salt, i.e. the cation or anion, and their valency. This was investigated by using a series of inorganic halides for the effects of cations and their valency, and a series of sodium salts for those of anions and their valency. Table I shows the salts employed.

Fig. 4a indicates the influence of univalent cations on the surface area. From the results, all the salts were found to decrease the surface area by their addition. Although cation properties such as the ionic radius might affect such a change, we were not able to determine which was the dominating one.

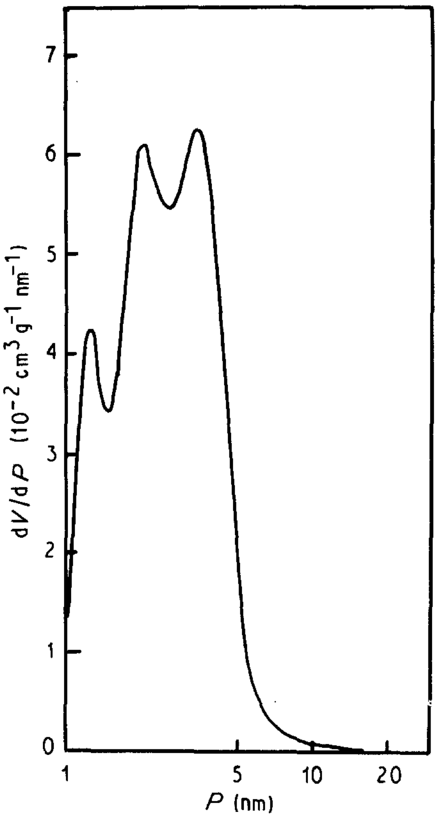

Figure 2 Pore size distribution of gel prepared by conventional sol–gel process, i.e. without additive.

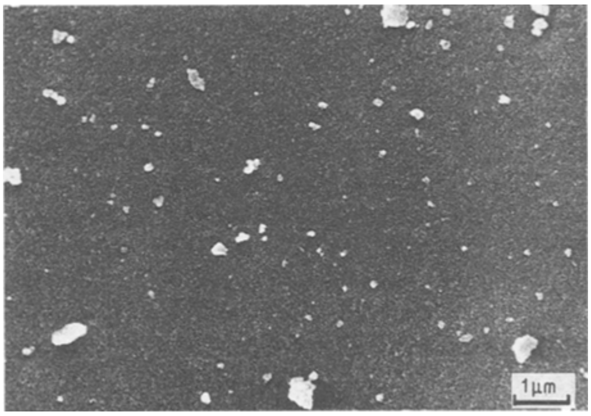

Figure 3 SEM image of gel prepared by conventional sol–gel process, i.e. without additive.

TABLE I Inorganic salts used as additives[a]

Valency	Cation	Anion
1	Li(Cl), Na(Cl), K(Cl), Cs(Cl)	(Na)Cl, (Na)Br, $(Na)NO_3$
2	$Mg(Cl_2)$, $Ca(Cl_2)$, $Ba(Cl_2)$	$(Na_2)SO_3$, $(Na_2)SO_4$
3	$Al(Cl_3)$, $In(Cl_3)$	

[a] Counter-anions and counter-cations are indicated by brackets.

Bi- and trivalent cations gave similar results. Fig. 4b shows the effects of anions on the surface area. A decrease in the surface area was again observed. In spite of several studies, the anion properties controlling the decrease could not be assigned.

Fig. 5 shows the relation between the surface area and the valency of the cation. The surface area decreased in the order of un- > bi- > trivalent cations.

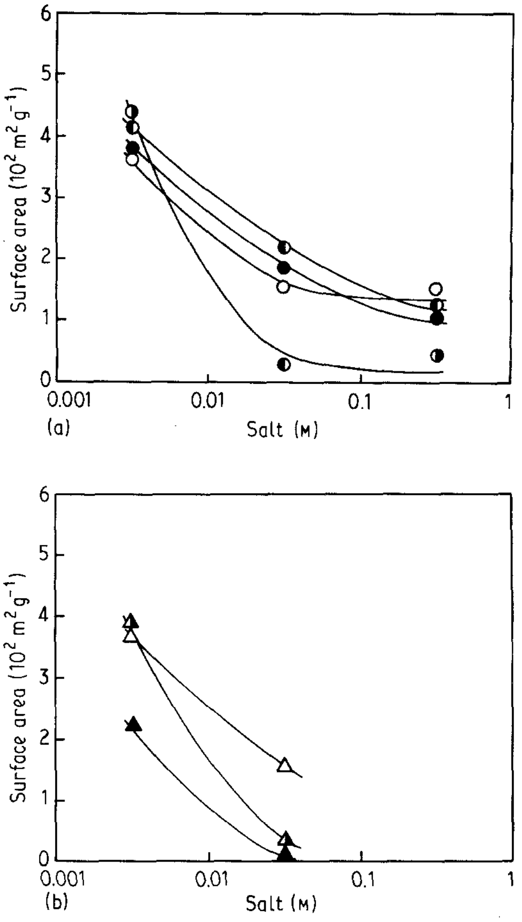

Figure 4 Change in surface area of gel by a modified sol–gel process using univalent (a) cations and (b) anions. Univalent cations (◑) Li, (◐) K, (○) Na, (●) Cs; anions, (◭) NO$_3^-$, (△) Cl$^-$, (▲) Br$^-$.

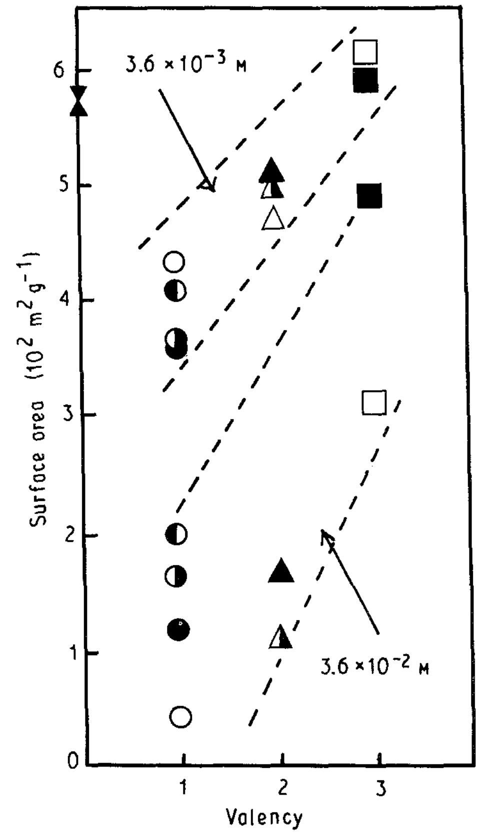

Figure 5 Dependence of surface area on the valency of cations: (○) Li, (◐) K, (●) Na, (◑) Cs, (▲) Ca, (◭) Ba, (△) Mg, (□) Al, (■) In.

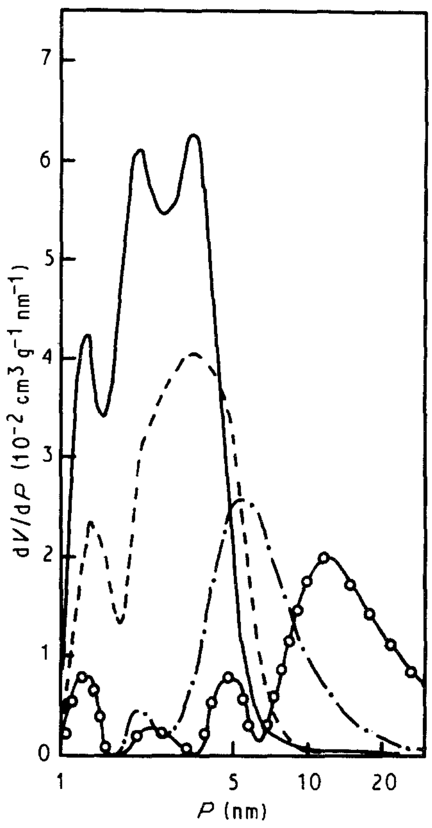

Figure 6 Pore size distribution of gels prepared with NaCl. Concentration of NaCl in starting solutions: (——) 0 M, (– – –) 2.5 × 10^{-4} M, (—·—) 2.5 × 10^{-3} M (○), 2.5 × 10^{-2} M.

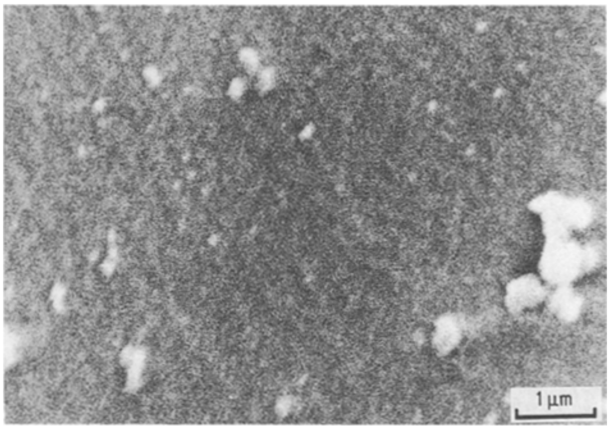

Figure 7 SEM image of gel prepared with NaCl. The concentration of NaCl in the starting solution was 0.08 M.

Thus, it was concluded that one of the factors changing the surface area was the valency of the cation.

The change in the surface area must influence the pore size distribution. Fig. 6 shows examples of such influence. By the addition of NaCl, the amount of mesopore decreased and the mean mesopore size increased slightly. Similar results were obtained for the other salts.

Fig. 7 shows an SEM image of a gel prepared by addition of NaCl. Macropores were not found on the surface. This salt, like the other salts, did not develop macropores under low salt concentrations, at least below 0.1 M.

3.2.2. Surfactant addition

Surfactants have several kinds colloidal property in aqueous solution: they aggregate above a critical micelle concentration (CMC) to make structures such as spherical micelles or lamellar structures by their hydrophobic interaction, and they adsorb to certain inorganic particles and influence the particles' interfacial properties. The sol–gel process involves colloidal solution. Thus, the addition of surfactants may affect the process so as to bring the desired gel. Table II shows the surfactants used. They differ in the charge of their head-group and in the alkyl chain length.

Fig. 8 shows the surface area of the gel as a function of the surfactant concentration. The surface area greatly changed according to the kind of the charge of the head-group of the surfactant. For the non-ionic surfactant Triton X-100, the surface area rose monotonously with the addition of surfactant. When the anionic surfactants DSS, SDS and STS were added, the surface area significantly decreased. On the other hand, addition of the cationic surfactants CTAB and DTAB caused a behaviour quite different from that for the anionic surfactants: the surface area passed through a minimum as the surfactant concentration rose. The surfactant concentration at the minimum was considerably different between CTAB and DTAB. The differences may be related to their difference in alkyl chain length.

Either surface activity or a salt effect of the surfactant must be responsible for the above behaviour with concentration change. For clarification, methylsulphuric acid (sodium salt) and ammonium chloride, respectively, were used as surface-inactive model compounds for anionic and cationic surfactants. In the case of the acid sodium salt, although the surface area decreased, it did not reduce to as low a value as with the anionic surfactants. Ammonium chloride gave only a small change in the surface area, which was quite different from the effect of cationic surfactants. Therefore, the surface activity of the cationic and anionic surfactants was probably responsible for the changes in surface area caused by their addition.

Fig. 9 shows the pore size distributions of gels prepared with Triton X-100. The gels had pore size distributions similar to that of a gel prepared by the conventional process. Greater addition of the surfactant developed a greater amount of large mesopores, but mesopores larger than 20 nm were not formed even at the highest concentration.

Fig. 10a and b show the pore size distributions of gels prepared with SDS and STS, respectively. For these anionic surfactants, pores corresponding to those formed by the conventional process decreased significantly, with instead a small development of large mesopores.

Fig. 11a and b show the pore size distributions of gels prepared with CTAB and DTAB, respectively. These cationic surfactants gave a behaviour quite distinct from that for the anionics. For both surfactants, the pores corresponding to those made by the conventional process decreased at first as the surfactant concentration increased gradually. Further addition of surfactant above a certain concentration developed small mesopores. This concentration almost agreed with the concentration at which the surface area shown in Fig. 8 began to increase. The

TABLE II Surfactants used as additives

Property	Surfactant
Anionic	Sodium decyl sulphate (DSS) Sodium dodecy sulphate (SDS) Sodium tetradecyl sulphate (STS)
Non-ionic	Polyoxyethylene(9.5) p-1,1,3,3-tetramethyl-butyl-phenol (Triton X-100)
Cationic	Decyltrimethylammonium bromide (DTAB) Hexadecyltrimethylammonium bromide (CTAB)

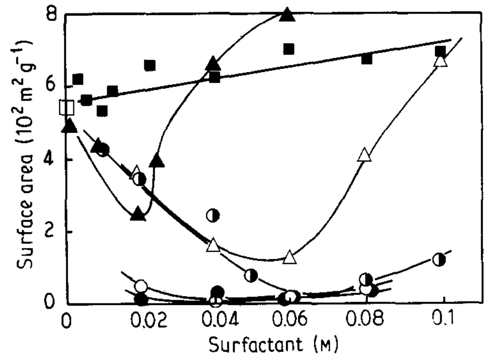

Figure 8 Change in the surface area of gel by addition of non-ionic, anionic and cationic surfactants. Non-ionic surfactant: (■) Triton X-100. Anionic surfactants: (○) DSS, (◑) SDS, (●) STS. Cationic surfactants: (▲) CTAB, (△) DTAB.

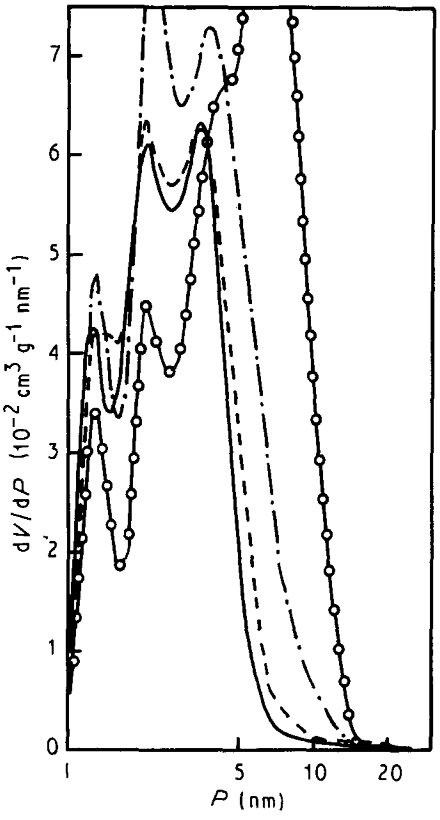

Figure 9 Pore size distribution of gels prepared with Triton X-100. Concentration of Triton X-100 in starting solutions: (——) 0 M, (– – –) 0.013 M, (— · —) 0.06 M, (○) 0.1 M.

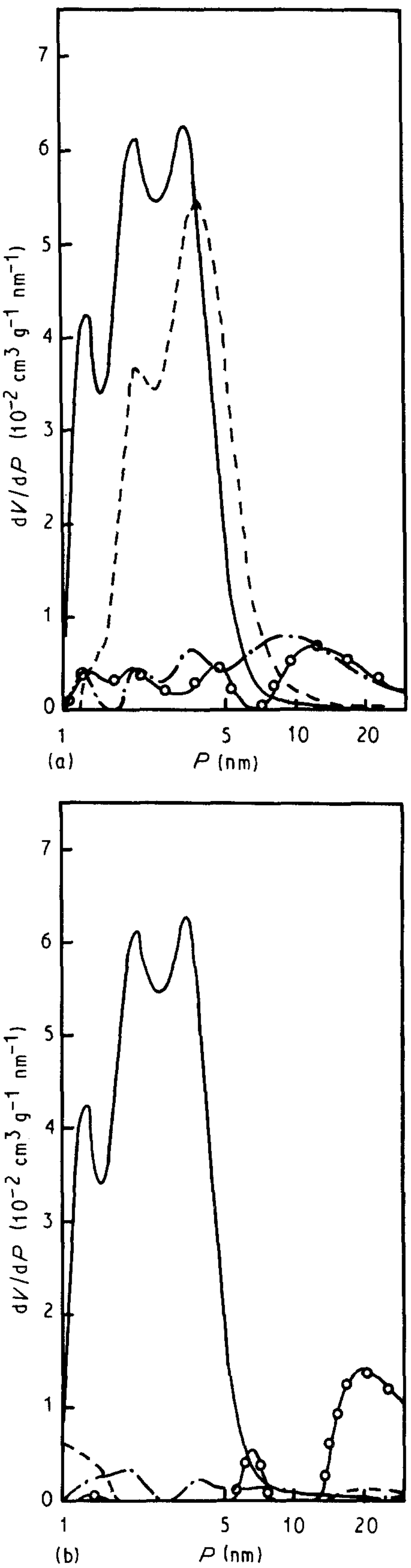

Figure 10 Pore size distribution of gels prepared with (a) SDS and (b) STS. Concentration of surfactant in (a): (——) 0 M, (– – –) 0.02 M, (—·—) 0.05 M, (○) 0.08 M, and in (b): (——) 0 M (– – –) 0.02 M; (—·—) 0.04 M, (○) 0.08 M.

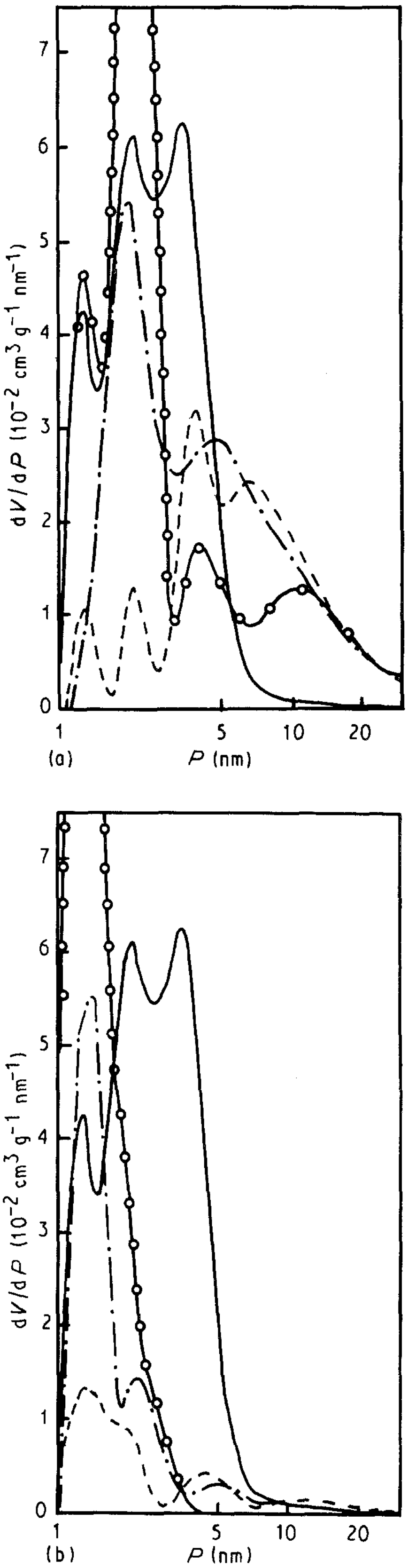

Figure 11 Pore size distribution of gels prepared with (a) CTAB and (b) DTAB. Concentration of surfactant in (a): (——) 0 M, (– – –) 0.02 M, (—·—) 0.025 M, (○) 0.06 M, and in (b): (——) 0 M, (– – –) 0.06 M, (—·—) 0.08 M, (○) 0.1 M.

increase in the surface area at high surfactant concentration was therefore considered to be due to the formation of small mesopores. The mean size of the small mesopores depended on the kind of cationic surfactant: CTAB gave pores distributing around 20 nm, while DTAB gave a size around 10 nm. The property, shown in Fig. 11, of distributing small mesopores in a narrow range suggests that the gels may have a regular structure.

Fig. 12a shows the X-ray diffraction patterns of gels prepared with CTAB, Triton X-100 and no additive. None of the diffraction patterns showed a peak except

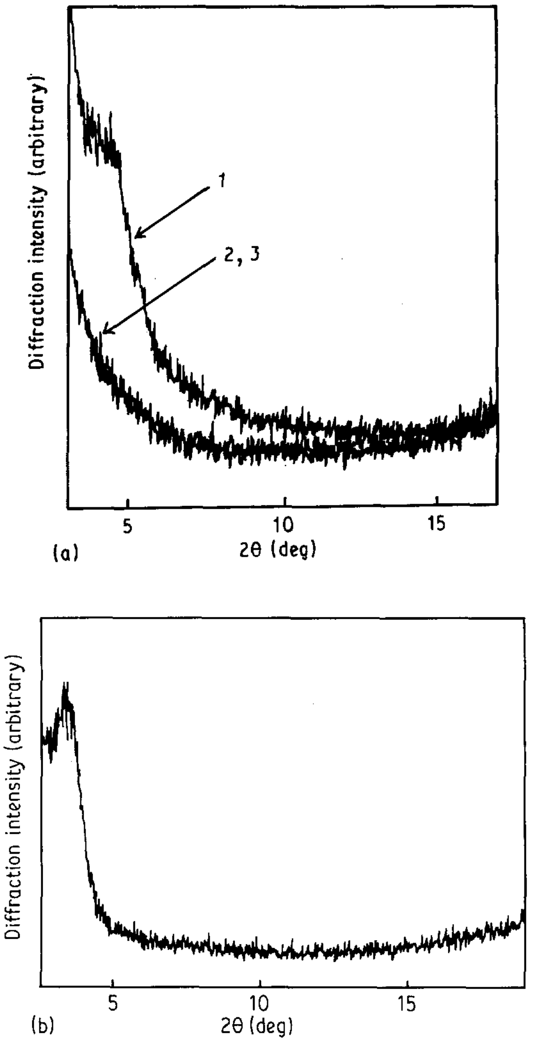

Figure 12 X-ray diffraction patterns of gels: (a) prepared with CTAB (curve 1), Prepared with Triton X-100 (curve 2), and without additive (curve 3); (b) prepared with DTAB. The concentration of surfactant in the starting solution was 0.1 M in all cases.

that the first gel, i.e. that prepared with CTAB, had a shoulder below 5°; thus the gels were almost amorphous. Fig. 12b shows the X-ray diffraction pattern of the gel prepared with DTAB. A definitive peak was found. Thus, the gels made with cationic surfactants were considered to have some regular structure.

Fig. 13a, b and c show the SEM images of the gels prepared with Triton X-100, SDS and CTAB, respectively. The gel prepared with the non-ionic surfactant Triton X-100 appeared to be similar to the gel prepared without additive, and had a flat surface and no macropores. In the case of SDS, the surface of the gel was uneven. The gel appeared to be densely aggregated with fine particles. Similar structures were also observed in the gels made with other anionic surfactants. In contrast to the above case, the gel prepared with CTAB had a bulky structure in which fine particles were loosely aggregated. A similar bulky structure was observed in the gel prepared with DTAB, though the size of the aggregating particles was different between the two gels.

4. Discussion

The sol–gel process starting from metal alkoxide is a colloidal process. During the formation of silica gel, intermediate silicates and sol particles are regarded as being present as ionic species, because a silica colloid particle has a charge except at the isoelectric point. The influence of inorganic salts on colloidal solutions containing charged particles can be evaluated by the Schulze–Hardy law: the coagulation stability of charged colloidal particles decreases with addition of ions having an opposite charge and an increase in the valency of the ions reduces the coagulation stability because they compress the electric double layer more around the charged particles when their valency is higher. Such a salt effect is expected to change the pore size distribution of the gel.

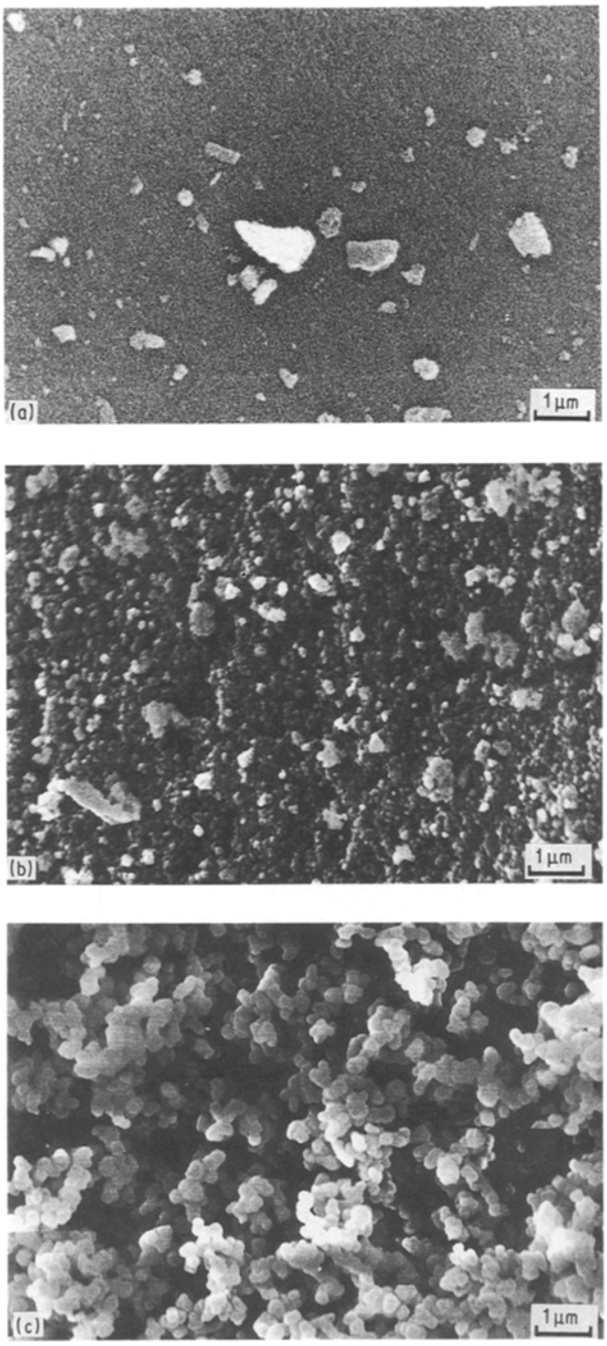

Figure 13 SEM images of the gels prepared with (a) Triton X-100, (b) SDS and (c) DTAB. The concentration of the surfactant in the starting solution was 0.08 M in all cases.

The salt addition resulted in changes that were as expected: the amount of mesopores corresponding to those produced by the conventional process decreased significantly and simultaneously the surface area reduced in almost all cases. Such behaviour depended mainly on the kind of cation of the salt used, and can be explained in terms of the property that silica usually has a negative charge. The magnitude of the influence was dependent on the cation valency as expected from the Schultze–Hardy law, and was in the order of uni- > bi- > trivalent cations. The order of influence, however, was different from that anticipated from the law. Therefore, besides the compression effect of the electric double layer around the ionic species, the cations must have brought about other effects which depressed the formation of mesopores.

When surfactants were used as additives, their influence was very different depending on the kind of charge of the head-group. Thus, different kinds of surfactant must have resulted in different effects. In the case of non-ionic surfactant the Triton X-100, the mesopores corresponding to those of the conventional process decreased a little while large mesopores were developed. The surface of the gel was flat by SEM measurement. These results were almost the same as those obtained with polyethylene glycol (PEG). The pore size distribution of mesopores also greatly resembled that obtained with PEG. Such a resemblance may be due to the structural resemblance that Triton X-100 bears to a polyethylene glycol chain. Triton X-100, however, is amphiphilic and is distinct from PEG which has hydrophilicity alone: it also has hydrophobicity owing to its hydrocarbon chain. This amphiphilicity was expected to have a different effect on the pore size distribution from that of PEG. As far as the present experimental results are concerned, the expectation was not met.

When anionic surfactants were used as additives, significant decreases in mesopores and corresponding decreases in the surface area were observed. The behaviour resembled that observed for inorganic salts. All the anionic surfactants used here had Na as a countercation, and Na probably acted in a similar way to that in the case of inorganic salt addition. Besides the Na action, however, another factor must participate in the behaviour: when the sodium salt of methylsulphuric acid, which is different from the anionic surfactants only in its alkyl chain length and does not have surface activity, was tested, it did not decrease the mesopores as much as the anionic surfactants. Therefore, the surface activity of the surfactants might participated in the above behaviour.

As shown in Fig. 11a and b, the addition of cationic surfactant caused a complicated change in the gel surface area and pore size distribution. Such behaviour was not observed for other additives. Two kinds of factor, at least, may be associated with such behaviour. The decrease of the mesopores at small additions of surfactant was likely to be caused by the same factor as in the addition of inorganic salts and anionic surfactants. The formation of small mesopores at greater additions of surfactant must be due to another factor: the surface activity of the surfactant plays an important role, because such small mesopore formation was found only with these surfactants. The pores of small size were distributed sharply for both surfactants. This result implies the presence of some regular pore structure in the gels. X-ray diffraction measurement revealed, in practice, the presence of some regular structure in the gels.

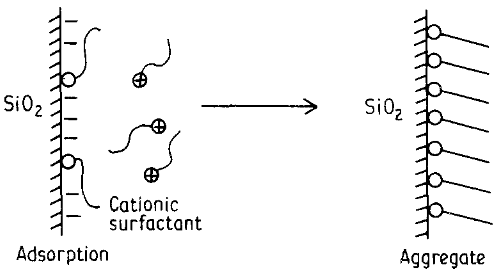

Figure 14 Possible mechanism for the formation of small mesopores.

Fig. 14 shows a possible mechanism for the formation of small mesopores. Since silicates are considered to have a negative charge, a cationic surfactant may adsorb to the silicate by electrostatic interaction and form aggregates by their hydrophobic interaction. The small pores may be formed in the removal process of the surfactants by calcination.

5. Conclusions

The pore size distribution of silica gels was controlled by application of the sol–gel process with the addition of several kinds of inorganic salt and surfactant. All the inorganic salts depressed the formation of mesopores. The influence was dependent upon the valency of the cation of the salt. When surfactants were used as additives, the influence was greatly dependent on the charge of their head-groups. Non-ionic surfactants slightly increased the large mesopores. The behaviour was explained in terms of the effect of the polyethylene glycol chain of the surfactants. Anionic surfactants greatly decreased the volume occupied by mesopores. Although their effects resembled those for inorganic salt addition, another factor attributable to their surface activity was presumed to participate. In the case of cationic surfactants, a small addition decreased the mesopores. However, further addition stimulated the formation of small mesopores. A stimulation mechanism was proposed.

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