Mixed Surfactant Assemblies in the Synthesis of Mesoporous Silicas

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MCM-41 type mesoporous silica material is synthesized, under mild conditions, in the presence of cetylpyridinium chloride as the templating species. Seven reflections become observable in the powder X-ray diffraction pattern of this material that can be indexed on the basis of a hexagonal close-packed unit cell with $a_o = 47.62$ Å. Synthesis of mesoporous silica materials is also demonstrated using self-assembling micellar aggregates of a mixture of two surfactants: cetylpyridinium chloride (CPCl) and cetyltrimethylammonium chloride (CTACl). As the CPCl:CTACl molar ratio between the two amphiphilic molecules decreases, a gradual increase in the d_{100}-spacing is observed starting at ca. 41 Å and in subangstrom increments reaching to that of ca. 43 Å. The materials were also characterized by DTGA, TEM, and Ar adsorption studies. A model is presented that simultaneously accounts for the higher degree of structural order of the mesoporous silica templated with CPCl and the ability to fine-tune d spacings on a subangstrom length scale using CPCl/CTACl mixtures.

Introduction

The discovery of the MCM41S family of mesoporous silicas[1,2] has led to a host of studies aimed at incorporation of transition metals into the structure of these materials for the purpose of tailoring catalytic activity[3,4] and creating novel composite materials by inclusion of a variety of guest species into the channels of the mesoporous silica host.[5,6]

Other studies have been carried out in an attempt to determine the mechanism of formation of these mesoporous siliceous materials[7−9] and to explore possibilities for fine-tuning the size of their pores. Controlling the mesopore size is of importance because of the potential applications of these materials as catalysts, molecular sieves, and hosts for quantum size effect electronic materials. Thus far, three ways have been demonstrated to tailor the pore sizes effectively. One has involved increasing the length of the alkyl chain of the surfactant molecule which leads to a larger diameter of templating micelles.[1] Another involves adding auxiliary organic molecules to the synthesis mixture.[1,10] Additives such as 1,3,5-trimethylbenzene dissolve in the hydrophobic region of the micelles causing their swelling which leads to larger pore sizes of the final products. The third technique involves the restructuring of the mesopores under mild aqueous conditions.[11] In essence, the aperture of the mesoporous channels can be enlarged in a controlled manner without any appreciable solubilization of the structure and loss of morphology of the starting materials.

We report here a new synthetic route for the preparation of mesoporous silica using cetylpyridinium chloride surfactant. Employing this surfactant in combination with cetyltrimethylammonium chloride in the synthesis mixture allows for the self-assembly of mixed micellar templates which give rise to materials with d-spacings tunable on a subangstrom length scale. The incentives for the use of CPCl in the synthesis of mesoporous silicas were that it is cationic, has a relatively similar aggregation number and cmc value as CTACl, yet allows for variation in the charge density at the headgroup. It is believed that interaction at the inorganic/organic interface is the most important factor in the formation of mesoporous silicas. The use of mixed micellar templates allows the possibility to gain a better understanding of how to control this interaction.

It was discovered that depending on the molar ratios of the two surfactants, tuning of the d spacings can be achieved in subangstrom increments, as observed

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through powder X-ray diffraction (PXRD) studies. The synthesis products display PXRD patterns exhibiting up to seven reflections that can be indexed on the basis of a hexagonal symmetry unit cell. This implies an improved degree of order of the mesopores. The PXRD reflections are found to be better resolved with a smaller full width at half-height (fwhh) than other patterns so far cited in the literature. As described below, these materials are characterized by DTGA, TEM, and Ar adsorption studies.

Experimental Section

Reagents used for the synthesis included TEOS (tetraethylorthosilicate, Aldrich, 98.99%), NH_4OH (Aldrich, 30 wt %), CPCl (Aldrich, used as supplied), and CTACl (29 wt % solution, Pflatz & Bauer, used as supplied). The synthesis of the silica-based mesoporous material was performed using the following reaction composition: 1 TEOS:9.2 NH_4OH:X CPCl:0.5 − X CTACl:130 H_20, where X varies as 0, 0.1, 0.2, 0.25, 0.3, 0.4, and 0.5. The resultant gel was treated at 80 °C for 3 days in polypropylene containers. The products were filtered, washed with deionized water, and then dried under ambient conditions. The as-synthesized materials were calcined in air at a rate of 1 °C/min reaching to a maximum of 540 °C. The synthesis mentioned above was repeated several times and all the data presented in this article have been consistently reproduced.

Powder diffraction data were obtained on a Siemens D5000 X-ray diffractometer using Ni-filtered Cu Kα radiation (λ = 1.541 78 Å). The PXRD patterns obtained with repeated synthesis show a variation in the d_{100} spacing of ca. 0.3 Å for a given reaction compostion. TEM images were obtained on a Phillips 430 microscope operating at 100 kV for which the samples were epoxy embedded, microtomed, and cut into 100−300 Å thin sections. DTGA experiments were performed on a Perkin-Elmer 7 Series Analyzer in which the samples were heated under N_2 at a rate of 5 °C/min. Argon adsorption at liquid argon temperature was performed on an Omnisorb system. BET surface area and pore volume for the samples were calculated subsequently from the entire argon adsorption data.

Results

The powder X-ray diffraction patterns of the as-synthesized and calcined mesoporous silica materials are shown in Figures 1 and 2. As-synthesized siliceous mesoporous materials have been known to have limited long-term structural stability. Basically, over a period of days to weeks, the materials show a gradual loss in intensity and a decrease in the d_{100} spacing as observed through PXRD. This can mainly be attributed to the fact that the siliceous framework is incompletely polymerized and undergoes a degradative process over time. For the as-synthesized materials, stored under ambient conditions, reported in this study, the PXRD patterns do not show any loss in intensity or shift in the d_{100} spacing over a period of 3 months.

The variations in the peak positions and fwhh in the PXRD patterns with the changes in the CPCl/CTACl ratio are shown in Figure 3. It can be seen that upon decrease of the CPCl/CTACl ratio in the reaction mixture the following changes in PXRD patterns occur. The d spacings and the peak intensities decrease and the fwhh of the observable peaks increases. The lowest angle peak (d_{100}) is observed at ca. 41 Å and gradually shifts to ca. 43 Å. These changes occur in a linear fashion. Additionally, the number of observable peaks also decreases from seven to five. Interestingly, the values of d spacings and the size of the composite CTACl−CPCL micellar template (that correlates with the effective length and relative concentrations of CTACl and CPCl in the synthesis mixture) are inversely proportional. The length of a CPCl molecule is ca. 23.7 Å and CTACl is 21.3 Å (see below).

Figure 4 displays the TEM micrographs of the calcined pure CTACl and CPCl templated mesoporous silicas. The SEM images of the as-synthesized materials display an average particle size of ca. 1 μm. The general trend suggested by PXRD is supported by the TEM study in that an increase in “order” of the pores is revealed with increasing the CPCl/CTACl ratio, CPCl-templated materials being the most ordered.

In Figure 5, the traces of the differential thermogravimetric analyses (DTGA) for three as-synthesized samples are shown. At 100% CPCl concentration in the reaction mixture, there is a diagnostic sharp peak at ca. 360 °C that can be assigned to loss of the cetylpyridinium surfactant (assignments were made using mass spectroscopy and DTGA control tests with pure surfactants). This peak is not present in the sample containing 100% CTACl whose diagnostic cetyltrimethylammonium surfactant loss occurs around 270 °C. In addition, it can be seen that the 270 °C peak is much broader at 100% CTACl concentration. Upon increasing the CPCl/CTACl ratio, the width of the peak appears to decrease. Furthermore, an interesting trend is observed at ca. 500°C. The broad band apparent in this region has been assigned to the loss of silanol groups present on the framework.[11] This band is only observed when CPCl is present in the reaction mixture and has an intensity that is proportional to the concentration of the surfactant. The corresponding peak for the sample synthesized only with CTACl is very sharp and occurs at ca. 340 °C.

Argon adsorption studies were performed using Olivier and Conklin’s density functional theoretical analysis.[12] This method is based on the statistical thermodynamics of a single inhomogeneous liquid phase having a density gradient near the pore surface. It is generally applicable to pore sizes covering the entire micro- to mesoporous size regime (3−500 Å). Primarily, the adsorption isotherms obtained for the calcined materials synthesized with different CPCl/CTACl ratios are all of type IV,[13] (Figure 6). In addition, the variation in pore volume as a function of pore width is shown in Figure 7. For the sample synthesized with 100% CPCl, the total pore area and pore volume were determined to be 962.7 $m^2\ g^{-1}$ and 0.940 $cm^3\ g^{-1}$ respectively.

Discussion

Upon increasing the stoichiometric mole fraction of cetylpyridinium chloride in the synthesis mixture, the synthesis products display PXRD patterns exhibiting up to seven reflections that can be indexed on a hexagonal symmetry unit cell (Figure 1). There is a corresponding improvement in uniformity of the pore structure of these mesoporous silicas as detected by TEM (Figure 4), and

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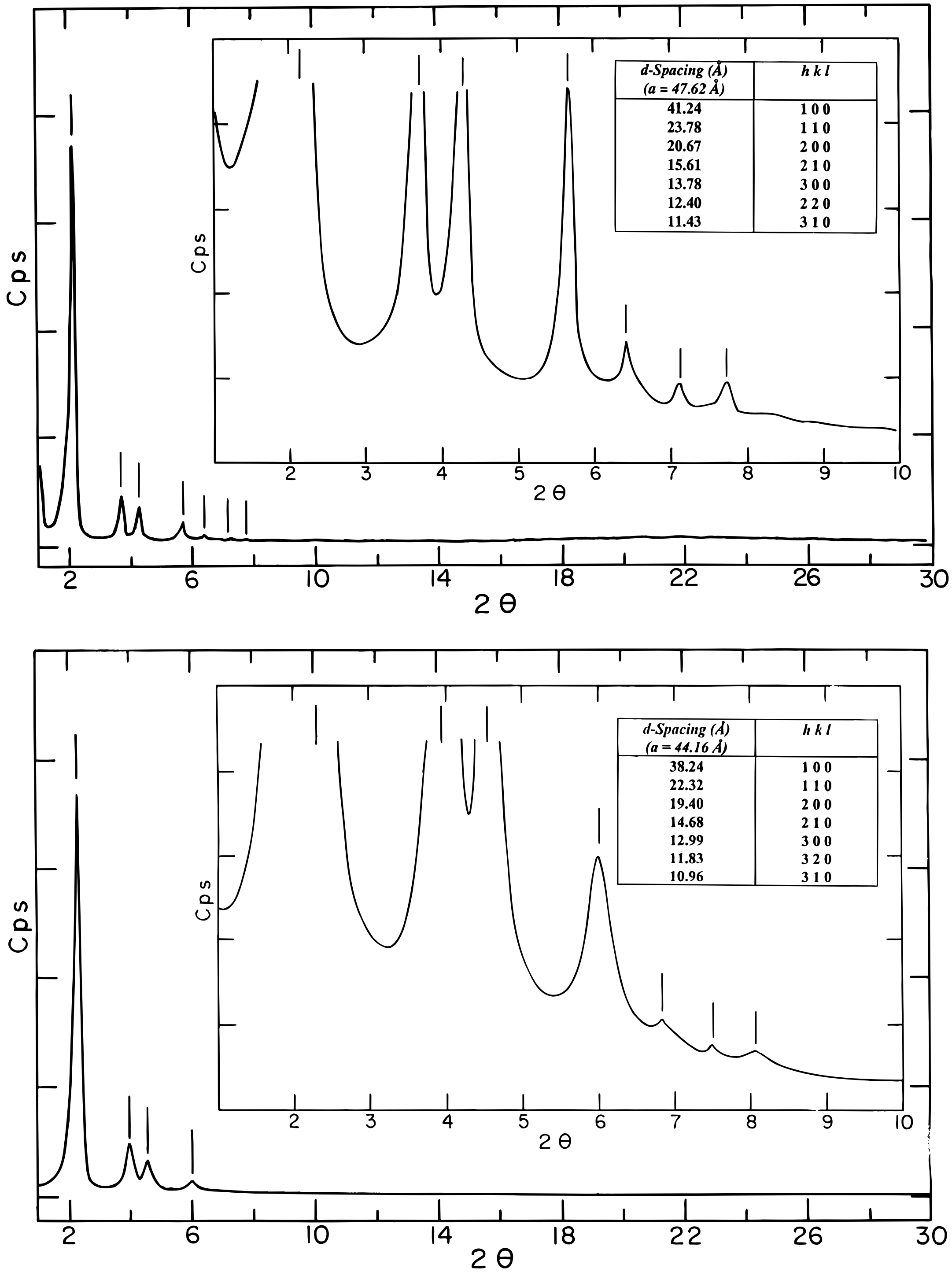

d-Spacing (Å) (*a* = 47.62 Å)	*h k l*
41.24	1 0 0
23.78	1 1 0
20.67	2 0 0
15.61	2 1 0
13.78	3 0 0
12.40	2 2 0
11.43	3 1 0

d-Spacing (Å) (*a* = 44.16 Å)	*h k l*
38.24	1 0 0
22.32	1 1 0
19.40	2 0 0
14.68	2 1 0
12.99	3 0 0
11.83	3 2 0
10.96	3 1 0

Figure 1. (a, top) PXRD pattern of mesoporous silica synthesized with a surfactant composition of 100 mol % CPCl. (b, bottom) PXRD pattern of calcined form of silica shown in (a).

determined by Ar adsorption that shows a gradual decrease in the width of pore size distribution with increasing fraction of CPCl in the mixture (Figure 7). This enhancement can be rationalized by a combination of factors, including the increased rigidity of CPCl micellar aggregates and stronger interaction between CPCl and silica. A key consideration is the smaller effective size of CPCl compared to CTACl micellar assemblies. This is purported to arise from the "folding-over" of the hydrophilic pyridyl-ring headgroup relative to the hydrophobic alkyl tail and the preferred tangential orientation of the pyridyl headgroup with respect to the micellar surface.[14] Consequently, the cationic quaternary nitrogen is more exposed to its polar surroundings and the resulting arrangement of surface pyridyl headgroups likely yields a more rigid and geometrically better-defined micellar template. It is also well documented that the preferred folded-over conformation of the pyridyl headgroup of CPCl favors a strong interaction between the quaternary nitrogen of the pyridyl ring and the surface of SiO_2.[14-16] Together, these effects likely result in a more well-

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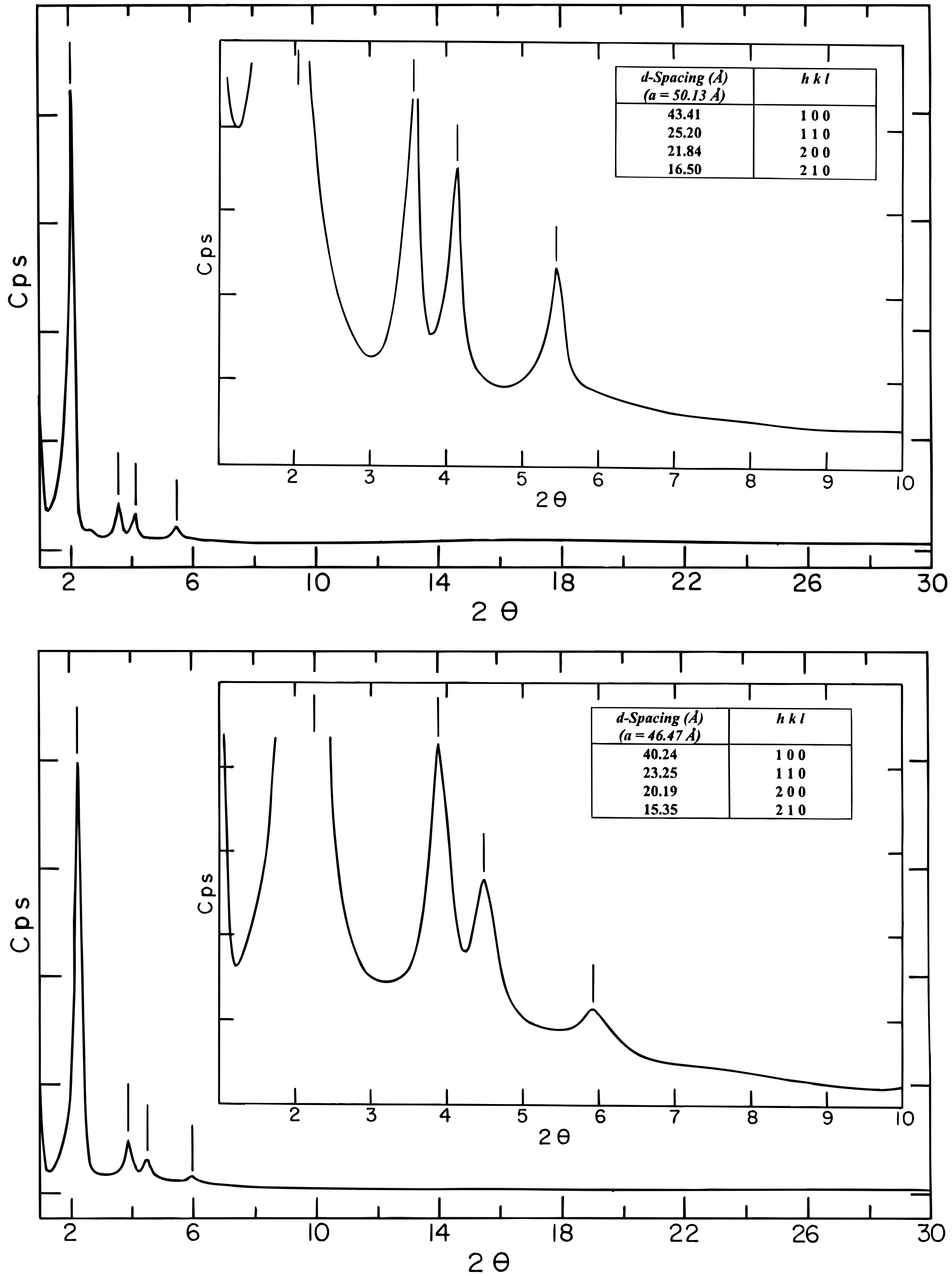

d-Spacing (Å) (*a* = 50.13 Å)	*h k l*
43.41	1 0 0
25.20	1 1 0
21.84	2 0 0
16.50	2 1 0

d-Spacing (Å) (*a* = 46.47 Å)	*h k l*
40.24	1 0 0
23.25	1 1 0
20.19	2 0 0
15.35	2 1 0

Figure 2. (a, top) PXRD pattern of mesoporous silica synthesized with a surfactant composition of 100 mol % CTACl. (b, bottom) PXRD pattern of calcined mesoporous silica shown in (a).

ordered co-assembly of the silica building-blocks and CPCl micellar template. Ultimately, this translates into an enhanced degree of long-range order of the mesopores.

For mixed micellar systems, several possibilities can be envisaged for their organization. Depending on the individual structure and charge of the amphiphilic molecules, the mixed micellar model can involve either ideal miscibility, total immiscibility or microscopic de-mixing.[17] In the ideal miscibility case, the mixed micellar composition is expected to be in accordance with the overall mixing ratio. In the case of complete immiscibility, repulsive interactions between the two surfactant structures should cause the presence of two different types of micellar structures (i.e., each corresponding to the two separate components). In microscopic de-mixing, a transition is expected to be present between the two extreme alternatives mentioned above. There exists the possibility that there is a simultaneous presence of micelles with different compositions. In

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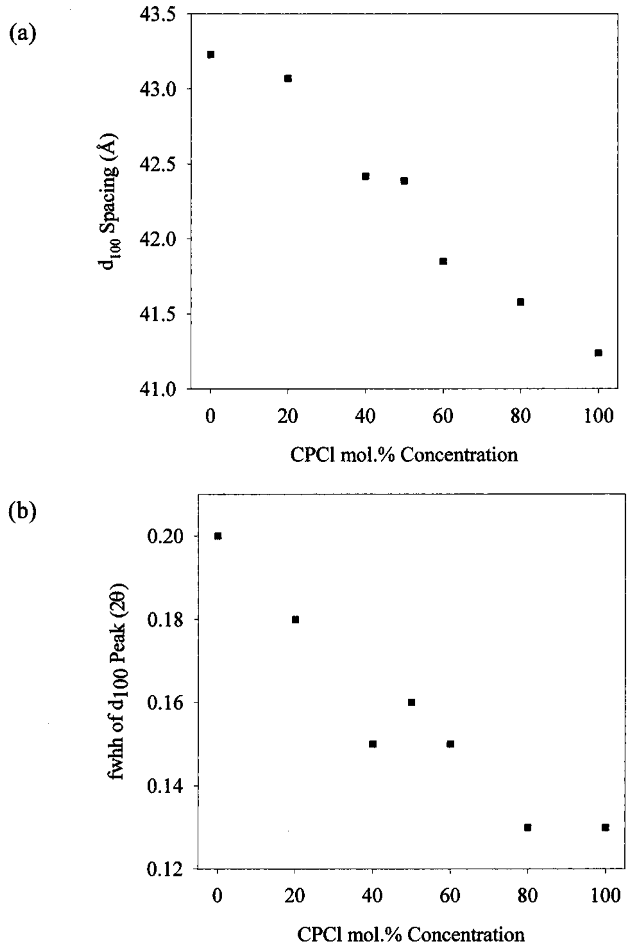

Figure 3. Variations in (a) d_{100} spacings and (b) fwhh versus the CPCl/CTACl ratio as determined by PXRD.

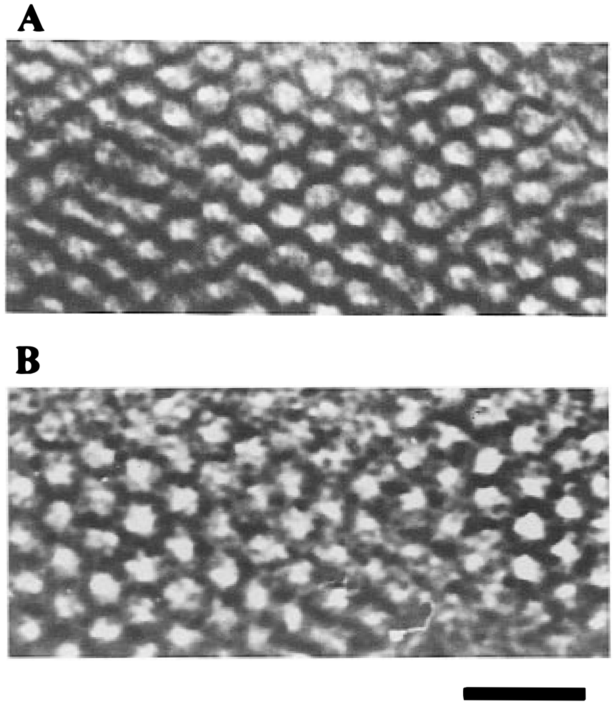

Figure 4. Representative TEM image of a calcined mesoporous silica templated with (a) 100 mol % CPCl and (b) 100 mol % CTACl. Scale bar = 10 nm.

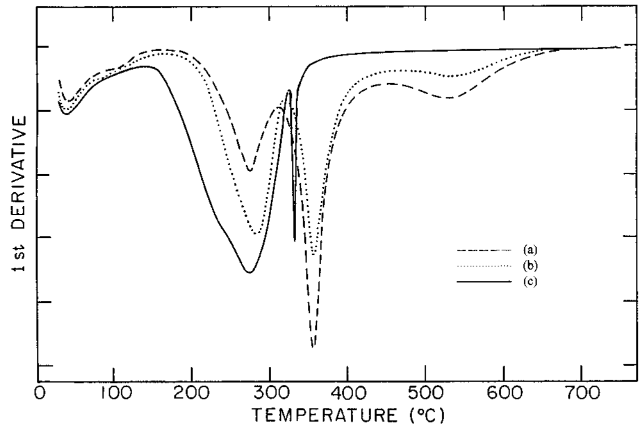

Figure 5. DTGA traces of as-synthesized samples of mesoporous silicas using (a) 100 mol % CPCl, (b) 50:50 ratio of CPCl: CTACl and (c) 100 mol % CTACl.

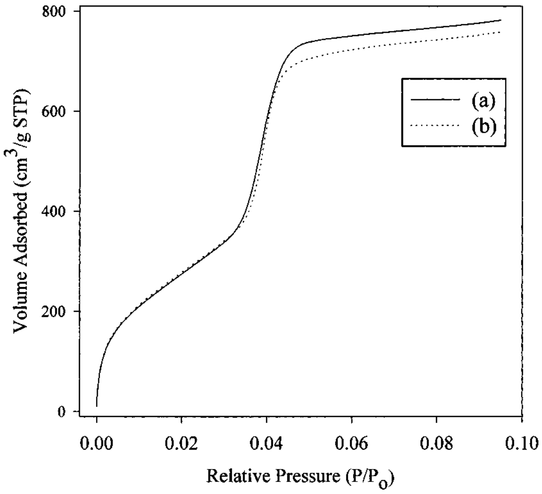

Figure 6. Argon adsorption isotherm for mesoporous silica sample synthesized with (a) 100% CPCl and (b) 100% CTACl.

addition, the formation of the above structures is dependent on the temperature, pH, concentration, mixing ratio, ionic strength, and the presence of other cosolvents.[17-19]

For the mixed CPCl/CTACl surfactant system being studied in this work, it has been shown by Nguyen et al.[19] that large deviations from ideal solution theory are not exhibited. This can be attributed to the similarity in counteranion, cationic headgroup charge, and hydrophobic chain length of CTACl and CPCl. Hence synergistic interactions between the two surfactant moieties can be assumed to control their mixing properties. The result of these interactions therefore suggests that the composition of the micelle in the mixed system is directly related to the concentration of the two amphiphilic structures in the solution. This is implied in the PXRD and DTGA data obtained in this study.

On the basis of the DTGA data, (Figure 5), there is a linear correlation between the area under the peak at ca. 360 °C (which solely results from loss of the cetylpyridinium surfactant) and the concentration of this surfactant used in the starting mixture. This suggests that in fact the amount of the two surfactants imbibed in the mesoporous materials correlates directly with their concentration in the starting mixture. In addition, it can be seen that the peak at ca. 270 °C decreases in

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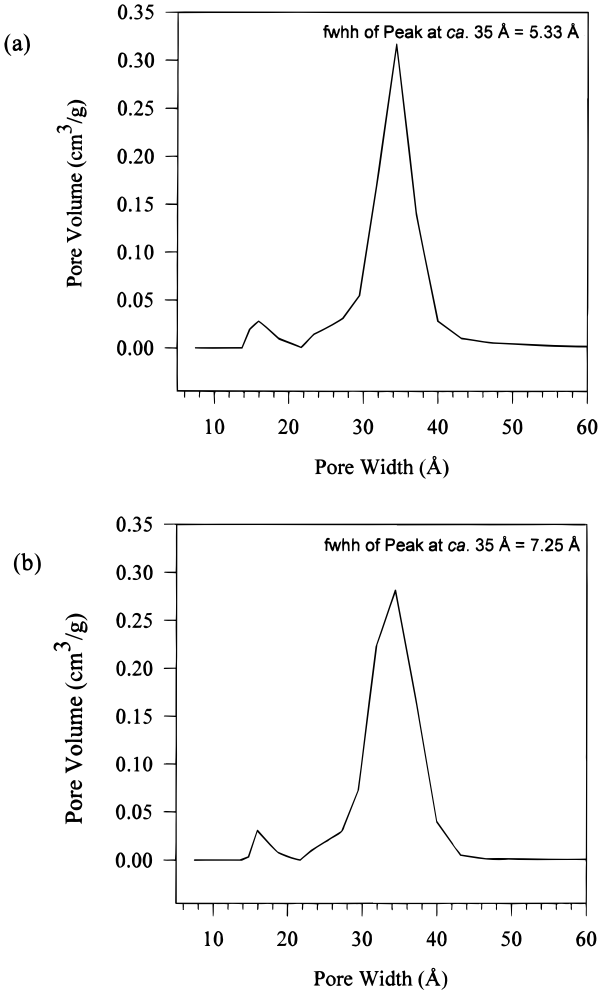

Figure 7. Pore volume values (as obtained from argon adsorption isotherms) as a function of pore width for calcined mesoporous silicas synthesized using (a) 100 mol % CPCl and (b) 100 mol % CTACl.

both area and width upon increasing the CPCl/CTACl ratio. This implies that upon incorporation of CPCl, the resultant micellar structure is ideally mixed and interactions between the silica and surfactant and within the surfactant phase become more uniform, thereby promoting a sharper thermal transition at 270 °C.

In the PXRD patterns of this study, there is an absence of two separate d_{100} peaks for samples involving the mixed surfactant templates. These peaks would be associated with the presence of separate domains in the structure of mesoporous silica products arising from the presence of two distinct micelle types in the synthesis mixture. The absence of such peaks suggests that in fact two separate micellar templates are not present. In addition, the observed decrease of the fwhh of the d_{100}-reflection (PXRD) with increasing CPCl/CTACl ratio has a linear rather than a nonlinear dependence. This implies that a singular-kind of micellar aggregate, whose composition is determined by the overall surfactant mixing ratio, is likely to be the templating moiety.

The linear trend in the d-spacings of the synthesized mesoporous silica materials with changes in the CPCl/CTACl ratio can therefore be rationalized according to the variation of the size of mixed micelles with respect to the CPCl/CTACl ratio. As mentioned above, it is believed that the pyridyl ring is folded-over relative to the hydrophobic alkyl chain in order to maximize the interaction of the cationic quaternary nitrogen with the anionic silica present. Upon increasing the concentration of CPCl in the synthesis mixture, the size of the resulting mixed micellar assembly decreases by becoming more “compact”. This is consistent with the observed linear decrease in the *d* spacing with increasing CPCl/CTACl ratio (Figure 3).

It should be noted that due to the limited resolution of the argon adsorption and TEM studies, it is difficult to make a definitive statement regarding trends in pore sizes with CPCl/CTACl ratio. Angstrom resolution transmission electron microscopy and adsorption studies need to be performed that will allow one to clarify whether the pore sizes are actually expanding.

Conclusions

The synthesis of mesoporous silicas with the CPCl surfactant has been demonstrated. It is believed that increased cooperative interactions between the pyridinium headgroup of the CPCl surfactant and silica building blocks is an essential factor for yielding materials that display an enhanced degree of order of the mesopores. In addition, this attribute together with the ideal miscibility of cetylpyridinium chloride and cetyltrimethylammonium chloride is usefully exploited to provide binary CPCl/CTACl micellar templates for the synthesis of mesoporous silicas having subangstrom precision tunable *d* spacing.

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