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# Low-Temperature Elimination of Organic Components from Mesostructured Organic−Inorganic Composite Films Using Vacuum Ultraviolet Light

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A novel and simple procedure named photocalcination has been developed for removing organic components from mesostructured organic−inorganic composite films. This procedure employs an excimer lamp radiating vacuum ultraviolet (VUV) light of 172 nm in wavelength. Organic molecules are removed through two distinct photochemical reactions proceeding simultaneously at room temperature: the photocleavage of C−H and C−C bonds in the organic molecules by direct photoexcitation and their subsequent oxidation with activated oxygen species generated by the photoexcitation of atmospheric oxygen molecules. In this study, a composite of cetyltrimethylammonium chloride−silica (CTAC−silica) was used. Thin films of this organic−inorganic composite were prepared on Si substrates coated with a self-assembled monolayer of octadecyltrimethoxysilane. The films were irradiated with VUV light under pressures of 10, $10^2$, $10^3$, or $10^5$ Pa. Although, in each case, the CTAC molecules in the composite films were completely oxidized and removed, the elimination rate increased with an increase in the photocalcination pressure. While 3 h of irradiation was necessary to completely remove the CTAC molecules at 10 Pa, only 0.5 h was required at $10^5$ Pa. However, the periodic mesostructures of the film photocalcined at $10^5$ Pa distorted significantly because of the rapid photooxidation. As a control experiment, identical CTAC−silica mesocomposite films were calcined thermally. The films were heated in air at temperatures from 373 to 773 K. Although the CTAC molecules could be eliminated completely at temperatures higher than 573 K, the periodic mesostructures of the thermocalcined films were much more distorted than those of the photocalcined films.

## 1. Introduction

Mesostructured materials, including mesoporous silica (MPS), fabricated using supramolecular templates of amphiphilic organic molecules have attracted much attention because of their potential applications, such as in filters,[1] sensors,[2] optoelectronic devices,[3] and optical waveguides.[4] To obtain arrays of ordered mesopores, such organic templates must be removed from the mesostructured organic−inorganic composites without distorting their fine structures. Other properties of the final mesostructured material are also markedly affected by methods of eliminating the organic templates.[5] Until now, calcination, a conventional method, has been generally applied. However, calcination promotes structural relaxation and damages the walls of the pores forming MPS.[6] In particular, when the composite is formed into a film on certain substrates, calcination leads to film shrinkage and generates a considerable amount of internal stress, resulting in distortion or even breakage of the film. Hence, an alternative method to eliminate organic templates at low temperature from as-synthesized organic−inorganic composite films has been strongly demanded. We have previously reported a novel calcination technique employing an excimer lamp radiating vacuum ultraviolet (VUV) light of 172 nm in wavelength.[7] This approach, which we have named photocalcination, allows the removal of organic molecules in organic−inorganic composite films at room temperature. Photocalcination

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[†] National Industrial Research Institute of Nagoya.

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(1) Ballew, H. W. *Am. Biotechnol. Lab.* **1997**, May, 8.

(2) (a) Sakai, H.; Baba, R.; Hashimoto, K.; Fujishima, A.; Heller, A. *J. Phys. Chem.* **1996**, *99*, 11896. (b) Tamagawa, C. Y.; Schiller, P.; Polla, D. L. *Sensors Actuators* **1992**, *A35*, 77.

(3) (a) Fendler, J. H. *Chem. Mater.* **1996**, *8*, 1616. (b) Rogers, J. A.; Bao, Z.; Makhija, A.; Braun, P. *Adv. Mater.* **1999**, *11*, 741. (c) Dag, Ö.; Ozin, G. A.; Yang, H.; Reber, C.; Bussière, G. *Adv. Mater.* **1999**, *11*, 474. (d) Honma, I.; Zhou, H. S. *Adv. Mater.* **1998**, *10*, 1532.

(4) (a) Yang, P.; Wirnsberger, G.; Huang, H. C.; Cordero, S. R.; McGehee, M. D.; Scott, B.; Deng, T.; Whitesides, G. M.; Chmelka, B. F.; Buratto, S. K.; Stucky, G. D. *Science* **2000**, *287*, 465. (b) Marlow, F.; Macgehee, M. D.; Zhao, D.; Chmelka, B. F.; Stucky, G. D. *Adv. Mater.* **1999**, *11*, 632.

(5) Moller, K.; Bein, T.; Fischer, R. X. *Chem. Mater.* **1999**, *11*, 665.

(6) Raman, K. N.; Anderson, M. T.; Brinker, C. *J. Chem. Mater.* **1996**, *8*, 1682.

(7) Hozumi, A.; Yokogawa, Y.; Kameyama, T.; Hiraku, K.; Sugimura, H.; Takai, O. *Adv. Mater.* **2000**, *12*, 985.

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is based on the photocleavage of C−H and C−C bonds in the organic molecules by direct photoexcitation and the subsequent oxidation of the decomposed organic molecules with activated oxygen species generated by VUV irradiation of atmospheric oxygen molecules.[8] Although extensive research on mesoporous materials has been reported in the literature, studies on the photochemical elimination of organic molecules have not been published. Our technique has undoubtedly great potential in its applicability to thermally unstable mesoporous materials, such as transition metal oxide and phosphate analogues.[9]

In this article, we report on the fabrication of MPS thin films from mesostructured organic−inorganic composites on the basis of photocalcination. First, mesostructured silica films were prepared by templating a liquid crystal micelle of cationic amphiphilic molecules. Next, these organic−silica composite films were photochemically calcined to remove their organic components and to obtain mesopores in the silica matrix. As described above, atmospheric oxygen plays a crucial role in photocalcination. Consequently, among the various experimental conditions for photocalcination, the atmospheric concentration of oxygen is of primary importance. We have, therefore, focused here on the effects of atmospheric pressure on the photocalcination of the composite films.

## 2. Experimental Section

**2.1. Substrates.** We prepared sample films, because distortion due to calcination appears more obviously in films than in powders, to investigate calcination damage to the periodic mesostructures in organic−inorganic composites. Among the various film synthesis methods so far reported, nucleation at the solid/water interface has been frequently employed to prepare mesostructured films.[10,11] In particular, on hydrophobic surfaces, such as graphite[10] and SAM-coated gold (SAM, self-assembled monolayer),[11] continuous films of mesostructured organic−silica composites were formed through hydrophobic and van der Waals interactions between the surfactant molecules and the hydrophobic surfaces. In our previous studies, we have prepared SAMs by the chemical vapor deposition (CVD) of octadecyltrimetoxysilane [ODS; $CH_3(CH_2)_{16}$-$CH_2Si(OCH_3)_3$)] on Si substrates covered with native oxide. The ODS−SAM's thickness as estimated by ellipsometry was $1.9 \pm 0.1$ nm and its surface was hydrophobic, showing a water contact angle of about 106°. We have grown a composite on such a surface as a continuous thin film.[12] Details of our CVD method have been described elsewhere.[13]

**2.2. Synthesis.** Composite film was synthesized on ODS−SAM/Si substrates in a solution prepared as follows. A mixture of CTAC (Tokyo Kasei Organic Chemicals), hydrochloric acid (HCl), and water ($H_2O$) was stirred for about 10 min until the CTAC powder completely dissolved. Tetraethoxysilane (TEOS, Tokyo Kasei Organic Chemicals) was then added to the solution and mixed while stirring for about 2 min at room temperature. The final reactant molar ratio of TEOS:CTAC:HCl:$H_2O$ was 0.1:0.11:7:100. Each of the substrates was immersed upside down in this solution and kept undisturbed at room temperature for 1 h. After immersion, the substrate was washed with Milli-Q water and blown dry with $N_2$ gas. The average film thickness measured by a profilometer (Model: SV-600, Mitsutoyo Co. Ltd.) was about 200 nm.

**2.3. Photo- and Thermocalcinations.** Two different methods were applied to eliminate CTAC molecules from the as-synthesized composite films to obtain mesopores. The first method, that is, photocalcination, was conducted as follows. A sample with a CTAC−silica composite film was placed in a vacuum chamber evacuated by a mechanical pump. The pressure in the chamber was maintained at 10, $10^2$, or $10^3$ Pa by introducing air through a variable leak valve or at $10^5$ Pa without evacuation.

The film was then irradiated for 0.5−5 h with an excimer lamp (Ushio Electric UER20-172V) at a distance of about 10 mm between the lamp window and the film surface. This excimer lamp radiates VUV light consisting of a single band centered at 172 nm in wavelength with a full width at half-maximum (fwhm) of 14 nm. Its power density is about 10 mW/$cm^2$ at the outside of the window. Because the excimer lamp radiates no infrared rays and, accordingly, does not heat the sample at all, this photocalcination is regarded to take place at room temperature.

Our second method applied conventional calcination to serve as a control experiment. Samples were treated inside a furnace installed with a programmable temperature controller. Its temperature increased at a rate of about 274 K/min to a predetermined temperature between 373 and 773 K and then remained here for 1 h. The samples were then allowed to cool spontaneously down to room temperature inside the furnace. This method is referred to as thermocalcination in this paper.

**2.4. Characterization.** The as-synthesized and calcined films were characterized by X-ray diffractometry using Cu K$\alpha$ radiation ($\lambda$ = 0.154 178 nm, XRD; MAC Science MXP$^3$), infrared transmission spectroscopy (IR; Biorad Laoratories FTS-175C), and X-ray photoelectron spectroscopy (XPS; AXIS HS, Shimadzu) using Mg K$\alpha$ radiation. The XPS X-ray source was operated at 10 mA and 12 kV. XPS depth profiles of the uncalcined and calcined films were obtained by Ar ion sputtering conducted at 150 mA and 3 kV.

## 3. Results and Discussions

Figure 1 shows IR transmission spectra of the CTAC−silica composite films before and after calcination. A typical spectrum of the uncalcined CTAC−silica film is indicated by spectrum (a) in which IR absorption bands can be seen at around 2850−2900 $cm^{-1}$ and at 1490 $cm^{-1}$. These bands are assigned to C−H stretching and C−H deformation vibrations of the CTAC molecules.[6] In addition, this spectrum shows peaks at around 1050 and 800 $cm^{-1}$ corresponding to Si−O−Si stretching and Si−O−Si deformation bonds and peaks at around 3000−3500 and 910 $cm^{-1}$ corresponding to Si−OH bonds. Furthermore, spectrum (a) displays a shoulder at around 1150−1200 $cm^{-1}$ because of the rocking vibration of $CH_3$ in the ethoxysilane [$Si(OEt)_n$, $n$ = 1, 2, 3] groups.[14] The uncalcined film is confirmed to be a composite of silica matrix and CTAC molecules. However, considering the shoulder at around 1150−1200 $cm^{-1}$, the silica in this composite is regarded as being polymerized organosilicate rather than pure $SiO_2$.

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[8] Holländer, A.; Klemberg-Sapieha, J. E.; Wertheimer, M. R. *Macromolecules* **1994**, *27*, 2893.

[9] (a) Stein, A.; Fendorf, M.; Jarvie, T. P.; Mueller, K. T.; Benesi, A. J.; Mallouk, T. E. *Chem. Mater.* **1995**, *7*, 304. (b) Cielsa, U.; Demuth, D.; Leon, R.; Petroff, P.; Stucky, G. D.; Unger, K.; Scuth, F. *J. Chem. Soc., Chem. Commun.* **1994**, 1387. (c) Knowles, J. A.; Hudson, M. J. *J. Chem. Soc., Chem. Commun.* **1995**, 2083.

[10] (a) Aksay, I. A.; Trau, M.; Manne, S.; Honma, I.; Yao, N.; Zhou, L.; Fenter, P.; Eisenberger, P. M.; Gruner, S. M. *Science* **1996**, *273*, 892. (b) Yang, H.; Kuperman, A.; Coombs, N.; Mamiche-Afara, S.; Ozin, G. A. *Nature* **1996**, *379*, 703.

[11] Yang, H.; Coombs, N.; Ozin, G. A. *Adv. Mater.* **1997**, *9*, 811.

[12] Sugimura, H.; Hozumi, A.; Ushiyama, K.; Takai, O.; Okido, M. *Trans. Mater. Res. Soc. Jpn.* **1999**, *24*, 449.

[13] (a) Hozumi, A.; Ushiyama, K.; Sugimura, H.; Takai, O. *Langmuir* **1999**, *15*, 7600. (b) Sugimura, H.; Nakagiri, N. *J. Photopolym. Sci. Technol.* **1997**, *10*, 661.

[14] (a)Deshmukh, S. C.; Aydil, E. S. *J. Vac. Sci. Technol.* **1995**, *A13*, 2355. (b) Hozumi, A.; Sekoguchi, H.; Takai, O. *J. Electrochem. Soc.* **1997**, *144*, 2824.

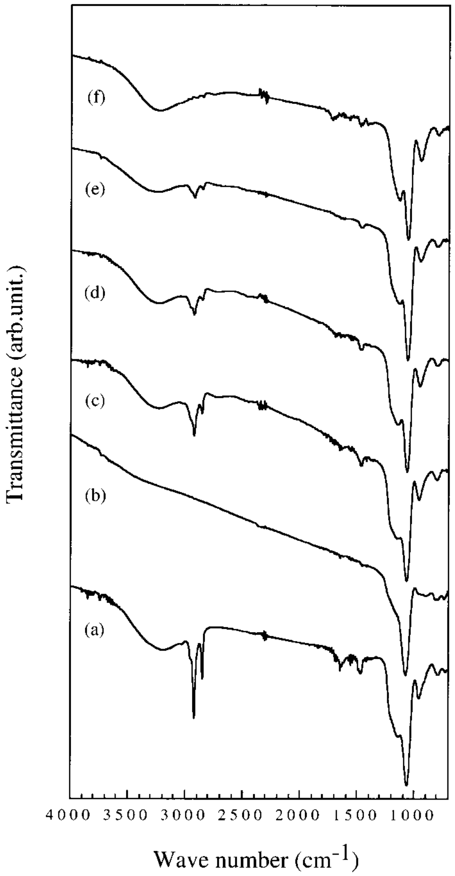

**Figure 1.** IR spectra of the composite films: (a) uncalcined, (b) thermocalcined for 0.5 h at 573 K, (c) photocalcined for 0.5 h at 10 Pa, (d) photocalcined for 0.5 h at $10^2$ Pa, (e) photocalcined for 0.5 h at $10^3$ Pa, and (f) photocalcined for 0.5 h at $10^5$ Pa.

**Table 1. Film Compositions before and after Photo- or Thermocalcination**

| compound (a/o) | Si | O | C | N | Cl |
|---|---|---|---|---|---|
| as-synthesized composite film | 23.1 | 19.4 | 50.3 | 3.2 | 4.0 |
| photocalcined MPS film (for 3 h at 10 Pa) | 34.6 | 55.9 | 6.0 | 2.1 | 1.4 |
| thermocalcined MPS film (for 1 h at 773 K) | 43.9 | 48.8 | 4.9 | 1.5 | 0.9 |

Spectrum (b) shown in Figure 1 is that of a film thermocalcined for 1 h at 573 K. The C−H bonds that were seen at around 2850−2900 and 1490 cm$^{-1}$ in spectrum (a) have completely vanished in spectrum (b). Furthermore, we confirmed by XPS that the C concentration of this film decreased markedly by about 88% because of thermocalcination, even at 573 K. Its C concentration was similar to that of a film thermocalcined at 773 K, as shown in Table 1.

Spectra of photochemically calcined films are also shown in Figure 1. Spectra (c)−(f) are those of films after photocalcination for 0.5 h at 10, $10^2$, $10^3$, and $10^5$ Pa, respectively. These spectra demonstrate that IR absorption peak intensities corresponding to C−H bonds decreased gradually with an increase in pressure during photocalcination. In particular, as shown in spectrum (f), the peaks completely disappeared after photocalcination at $10^5$ Pa. Even at the reduced pressures of 10, $10^2$, and $10^3$ Pa, when photocalcination was extended to 3, 2, and 1 h, respectively, the C−H absorption peaks disappeared, indicating the elimination of all the CTAC molecules. Photocalcination was found to be effective for eliminating the CTAC molecules from the composite films. The typical XPS results shown in Table 1 are in good agreement with our IR results. Elimination accelerated with an increase in atmospheric pressure. However, it is unclear why the elimination rate at $10^5$ Pa was only 6 times faster than that at 10 Pa. It is reported that the transparency of VUV light at $10^5$ Pa is about 10% and that the rest is absorbed by oxygen molecules in the atmosphere, resulting in the formation of activated oxygen atoms.[15] Thus, the amount of activated species at $10^5$ Pa is thought to be about $10^4$ times larger than that at 10 Pa. Considering the actual elimination rates obtained in the photocalcination, the diffusion of these activated oxygen atoms into the film appears to be too slow and was considered as a rate-determining step. Most of the activated oxygen atoms in the atmosphere were not involved in the photooxidation. Therefore, the actual elimination rate became much lower than the elimination rate expected for that oxygen concentration. It is noteworthy that the absorption intensities due to Si−OH bonds around 3000−3500 and 910 cm$^{-1}$ seen in spectra (c)−(f) of the photochemically calcined films are stronger than those seen in spectrum (b) for the thermocalcined film. A considerable amount of silanol groups are thought to remain in the MPS films prepared by photocalcination, probably on the mesopores' walls, because the photocalcination was conducted at room temperature. Silanol groups on silica surfaces are known to decrease at higher temperatures.[16]

To investigate the homogeneity of the photocalcined films, depth profiles of their C, N, Cl, Si, and O concentrations were measured by XPS. Figure 2 a shows a typical depth profile of the uncalcined composite film. The C concentration is almost constant inside the film at about 50.3 a/o. The concentrations of Si and O are about 23.1 and 19.4 a/o, respectively. The depth profile of the photocalcined film seen in Figure 2b has a smaller C concentration of about 6.0 a/o. This demonstrates that carbon components were effectively removed from the composite film by photocalcination. However, the remaining carbon concentration of the photocalcined film, as shown in Table 1, is not small enough to allow us to conclude that the carbon components were completely eliminated. The carbon concentration may further decrease if the VUV irradiation time were increased. However, considering that some amount of carbon, that is, about 5 a/o, was still detected in the film thermocalcined, even at 773 K, any further decrease in carbon concentration may be minute, even if photocalcination were further prolonged. We believe that the detected carbon may have been derived from oxidized products, that is, CO and $CO_2$. Parts of these probably adsorbed on the silica walls and did not diffuse out.

All of the elements observed in the depth profile of the photocalcined film are almost homogeneously distributed throughout the film. This indicates that our photochemical approach succeeded in uniformly eliminating the organic components from the composite films.

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(15) Sugimura, H.; Shimizu, T.; Takai, O. *J. Photopolym. Sci. Technol.* **2000**, *13*, 69.

(16) (a) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710. (b) Sneh, O.; George, S. M. *J. Phys. Chem.* **1995**, *99*, 4639.

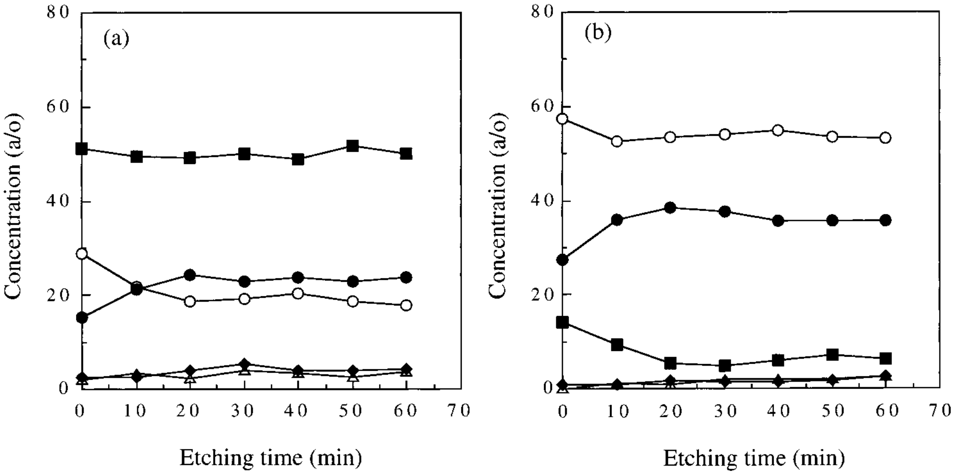

**Figure 2.** XPS depth profiles of the composite films: (a) uncalcined and (b) photocalcined for 3 h at 10 Pa. ■, C; ○, O; ●, Si; ◆, Cl; △, N.

It is evident that the VUV light penetrated the 200-nm-thick composite film and the photodecomposed products sufficiently diffused out.

Chemical compositions of the uncalcined, photocalcined, and thermocalcined films are summarized in Table 1. The C concentrations of both the calcined films decreased markedly. The organic components were efficiently removed from the composite films by both calcination methods. It is noteworthy that the O/Si ratio of the photocalcined film is 1.6, while that of the thermocalcined film remained little changed at 1.1. Although thermocalcination was performed at a pressure of $10^5$ Pa, at which a sufficient amount of oxygen was expected to be supplied, the silica walls of the thermocalcined film were much less oxidized than those of the film photocalcined at 10 Pa. At this pressure, the amount of oxygen supplied was extremely low. The photochemical reactions induced by the VUV light are thus considered to play an important role in oxidation of the silica walls.

Here, we discuss the photocalcination mechanism. VUV light of 172 nm in wavelength dissociatively excites chemical bonds (e.g., C−C, C−H, and Si−C) and decomposes organic molecules.[8] Moreover, VUV light between 133 and 200 nm can dissociate $O_2$ and generate excited oxygen atoms at several excited states [i.e., $O(^1D)$ or $O(^1S)$] as well as ground-stated atoms [$O(^3P)$].[17] When the composite films are irradiated with the VUV light in the presence of atmospheric oxygen, the two distinct photochemical reactions described above proceed simultaneously in the atmosphere. Because these activated oxygen species have strong oxidative reactivity to organic molecules, the organic molecules that have been decomposed as a result of the direct VUV excitation further react with these activated species and are finally converted to volatile products such as CO, $CO_2$, $NO_x$, and HCl.[18] Thus, the elimination rate of the organic components is strongly dependent on the oxygen concentration in the atmosphere. The silica walls of the as-synthesized film are polymerized organosilicate rather than inorganic oxide. When this organosilicate is irradiated with the VUV light, its organic components as well as the surfactant molecules are decomposed. The activated oxygen species may further oxidize the silica walls. This is the most likely reason, even at 10 Pa, the photocalcined silica walls were more completely oxidized.

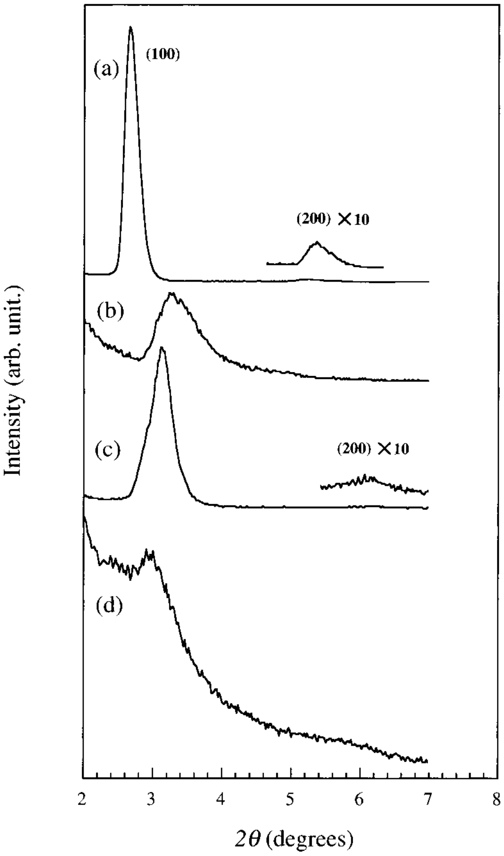

**Figure 3.** XRD traces of the composite films: (a) uncalcined, (b) thermocalcined for 1 h at 573 K, (c) photocalcined for 3 h at 10 Pa, and (d) photocalcined for 0.5 h at $10^5$ Pa.

Figure 3 shows typical XRD patterns of uncalcined (a), thermocalcined (b), and photocalcined (c and d) composite films. Both trace (a), for the uncalcined film, and trace (c), for film photocalcined for 3 h at 10 Pa, indicate one intense (100) diffraction peak with a weak

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[17] (a) Inoue, K.; Michimori, M.; Okuyama, M.; Hamakawa, Y. *Jpn. J. Appl. Phys.* **1987**, *26*, 805. (b) Amimoto, S. T.; Force, A. P.; Gulotty, R. G., Jr.; Wiesenfeld, J. R. *J. Chem. Phys.* **1979**, *71*, 3640.

[18] Ishikawa, Y.; Yoshima, H.; Hirose, Y. *J. Surf. Finish Soc. Jpn.* **1996**, *47*, 74.

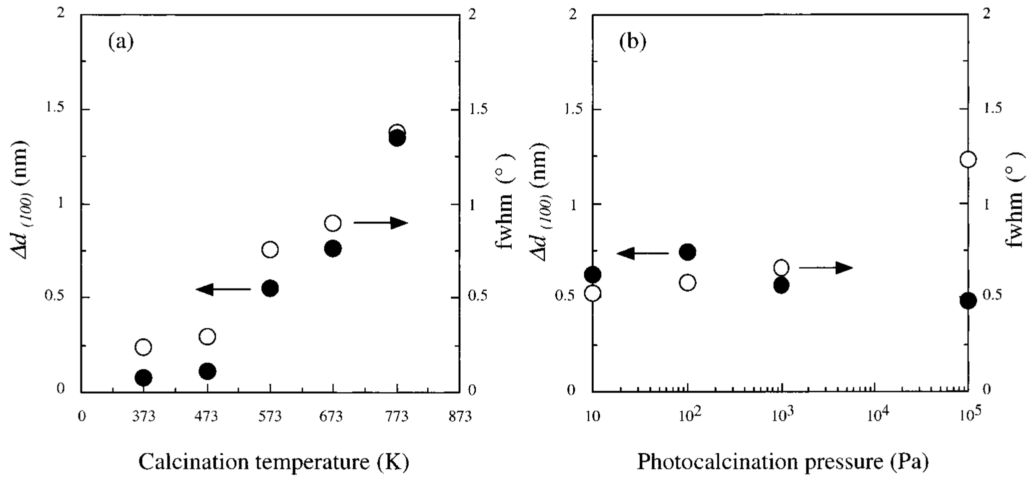

**Figure 4.** Differences between the *d* values ($\Delta d_{100}$, solid circles) before and after (a) thermocalcination and (b) photocalcination plotted together with the fwhm (open circles) of the MPS film's (100) peaks for the same.

(200) peak. The absence of (110) and (210) reflections in these XRD patterns indicates that the channel axis of the hexagonal unit cell is oriented parallel to the ODS–SAM/Si surface.[10,16] A steady decrease in the $d_{100}$ spacing as well as a decrease in the intensity of the (100) peak can be observed in trace (c). Nevertheless, the hexagonal structure still remains, even after elimination of the organic molecules. In contrast, the intensity of the (100) peak in the XRD trace (d) of the film photocalcined for 0.5 h at $10^5$ Pa has decreased markedly and the (200) peak is undetectable. These indicate that the mesostructure of this film is more disordered. The film thermocalcined at 573 K [trace (b)] and the films photocalcined for 2 h at $10^2$ Pa and for 1 h at $10^3$ Pa (not shown) were similarly disordered as confirmed by their XRD patterns.

Initial $d_{100}$ values of the uncalcined CTAC–silica composite films were in the range of 3.2–3.7 nm. Differences between the $d_{100}$ values ($\Delta d_{100}$) before and after thermo- or photocalcination under various calcination conditions were measured for each sample. As shown in Figure 4 (a), $\Delta d_{100}$, as indicated by the solid circles, increased markedly after thermocalcination at temperatures higher than 473 K. After thermocalcination at 773 K, $\Delta d_{100}$ was about 1.3 nm, indicating that the $d_{100}$ had decreased by about 36%. The fwhm of the thermocalcined films' (100) peaks indicated by the open circles also increased. The greater distortion of the mesostructures in the thermocalcined film was probably caused by water contained in the film. It has been reported that as-synthesized or incompletely polymerized silica mesostructures containing moisture were greatly distorted by thermocalcination.[19] This was ascribed to hydrolysis of the Si–O–Si bonds in the silica matrix at high temperature. However, well-ordered mesopores were obtained by means of thermal dehydration in a vacuum prior to thermocalcination.

In contrast, as shown in Figure 4b, there was little change in the $\Delta d_{100}$ (solid circles) after photocalcination at pressures from 10 to $10^3$ Pa. However, the fwhm (open circles) of the photocalcined film's (100) peaks increased markedly at $10^5$ Pa (1.23°). This value is larger than that of the film thermocalcined at 573 K (0.76°). This larger distortion of the film photocalcined at $10^5$ Pa is probably due to rapid photooxidation. In such a case, a considerable amount of activated oxygen species is formed by VUV irradiation. These active species may react with organic molecules, resulting in the formation of volatile products, such as CO, $CO_2$, or $NO_x$. When the decomposed organic species are rapidly eliminated from the composite films as such volatile species, the walls of the pores might break because of a marked increase in internal pressure. Therefore, photocalcination performed at $10^5$ Pa caused great damage and distortion to the composite films. Thus, we conclude that 10 Pa serves as an optimum pressure to supply activated oxygen species for the complete photodecomposition of organic molecules without distorting mesostructures.

## 4. Conclusions

Low-temperature elimination of organic molecules from CTAC–silica composite films was demonstrated using an excimer lamp radiating VUV light of 172 nm under various atmospheric pressures. The results presented here indicate that the photocalcination pressure is of primary importance in this process. The CTAC molecules in the composite films were eliminated completely during photocalcination conducted over the pressure range of 10–$10^5$ Pa at room temperature. The elimination rate was strongly dependent on the atmospheric pressure and increased as pressure did from 10 to $10^5$ Pa. The rate at $10^5$ Pa was approximately 6 times faster than that at 10 Pa. The photodecomposition mechanism of the organic components in the composite films is concluded to be the dissociative excitation of the organic molecules and the subsequent oxidation reaction with activated oxygen species generated by VUV irradiation of atmospheric oxygen molecules. However, distortion of mesostructures was greater at $10^5$ Pa, probably because of the rapid formation of volatile products, resulting in a significant increase of internal pressure inside the mesopores. To preserve the periodic mesostructures, an atmospheric pressure of 10 Pa is considered optimum for the photocalcination process. Identical CTAC–silica mesocomposite films were thermocalcined at temperatures from 373 to 773 K. CTAC

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(19) (a) Yang, H.; Coombs, N.; Ozin, G. A. *J. Mater. Chem.* **1998**, *8*, 1205. (b) Tatsumi, T.; Koyano, K.; Tanaka, Y.; Nakata, S. *Chem. Lett.* **1997**, 469.

molecules were eliminated completely at temperatures higher than 573 K; however, mesostructures of these films were much more distorted than those in the photocalcined films. In addition, despite the successful reduction of organic components in the thermocalcined films, oxidation of the silica walls was much less than that achieved with the photocalcined films.

The principal advantages of photocalcination for its further application can be summarized as follows. First, distortion of the mesostructures is much smaller than that with thermocalcined MPS films. Considering the application versatility of MPS thin films, it is of primary importance to precisely control pore size and preserve mesostructure integrity. Second, because this process allows the elimination of organic molecules at around room temperature, photocalcination is applicable to thermally unstable mesoporous materials. Third, the process uses no organic solvents. Fourth, it requires only a relatively short treatment time. Finally, our approach is also advantageous for additional modification of MPS because a considerable amount of silanol groups remain on the silica walls. These can serve as anchoring points for silane coupling reagents having a wide variety of functional groups, for example, phenyl, octyl,[20] thiol, amine, epoxide, imidazole, allyl,[21] and vinyl groups.[22] However, photocalcination requires special and expensive apparatus, including the vacuum chamber and excimer lamp, and the method is limited to the calcination of VUV light-permeable mesocomposites.

Because this process depends on the photoinduced cleavage of C−C and C−H bonds and the consequent decomposition of organic molecules, we are currently extending this photocalcination technique to the elimination of other organic molecules including block copolymers and emulsions.

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(20) Burkett, S. L.; Sims, S. D.; Mann, S. *Chem. Commun.* **1996**, 1367.

(21) (a) Fowler, C. E.; Burkett, S. L.; Mann, S. *Chem. Commun.* **1997**, 1769. (b) Lim, M. H.; Blanford, C. E.; Stein, A. *Chem. Mater.* **1998**, *10*, 467. (c) Mercier, L.; Pinnavaia, T. J. *Adv. Mater.* **1997**, *9*, 500. (d) Feng, X.; Fryxell, G. E.; Wang, L.-Q.; Kim, A. Y.; Liu, J.; Kemner, K. M. *Science* **1997**, *276*, 923. (e) Liu, J.; Feng, X.; Fryxell, G. E.; Wang, L.-Q.; Kim, A. Y.; Gong, M. *Adv. Mater.* **1998**, *10*, 161.

(22) Lim, M. H.; Blanford, C. E.; Stein, A. *J. Am. Chem. Soc.* **1997**, *119*, 4090.