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Adsorption of Methylene Blue onto Aluminum-Containing Mesoporous Silica Films Prepared by Rapid Solvent Evaporation Method

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The adsorption of methylene blue onto aluminum-containing mesoporous silica films was investigated. The mesoporous silica films were synthesized by rapid solvent evaporation method using tetramethoxysilane, aluminum tri(*s*-butoxide), and trimethyloctadecylammonium chloride as a silica source, alumina source and supramolecular template, respectively. Methylene blue was adsorbed effectively on the mesoporous silica films from solutions. The adsorbed amount increased with the increase in the aluminum content of the films, indicating that the added aluminum generated the adsorption sites (probably acidic sites) for methylene blue adsorption. The mesopore surface is not strongly acidic because the protonation of methylene blue did not occur. Adsorbed methylene blue exists as monomers in the mesopore. The dehydration of the films resulted in the aggregation of methylene blue, as evidenced by the visible absorption spectra.

The cooperative assemblies of surfactants and soluble inorganic species have been utilized to construct nanostructured inorganic–organic hybrid materials. Nanoporous materials obtained by the cooperative assembly and subsequent template removal have been investigated from both fundamental and practical viewpoints owing to their unusually high surface area and porosity, ordered pore arrangements, pore size uniformity, as well as possible surface engineering. Nanoporous silicas with variable pore size and geometry became available by selecting synthetic conditions such as surfactant structures and concentrations. Efforts have also been made in order to apply nanoporous silicas as adsorbents, and as catalysts and their supports, and in host–guest chemistry.

The morphology of nanoporous silicas is a key issue for their practical applications as well as for understanding the formation mechanisms of inorganic-surfactant hybrid mesostructures. Thin films are ideal for the applications to optical, electronic, and sensing devices as well as separations. We have successfully synthesized mesostructured thin films composed of silica-alkyltrimethylammonium salts by depositing a precursor solution containing surfactant and a soluble silica precursor derived from alkoxysilanes (solvent evaporation method).[1,2] In 1996, thin films of silica-alkyltrimethylammonium salts mesostructured materials were also prepared by nucleation on solid substrates and at air–water interfaces.[3–5] Motivated by these successes, many researchers have studied the syntheses of silica-surfactant mesostructured materials and their conversion to mesoporous silica films.[6–17] Among possible approaches, the solvent evaporation method has become a versatile technique for the fabrication of silica-surfactant mesostructured materials due to the ease of synthetic operation and the homogeneity and quality of the resulting materials.[18–24]

Taking advantage of the characteristic features of the mesoporous silica films, we have been interested in the immobilization of organic photoactive species in the mesostructured materials, which would become photofunctional materials in the future. The incorporation of organic dyes into thin films of silica-surfactant mesostructured materials[25–29] as well as mesoporous silica films[30,31] has been reported so far. The ways to introduce guest species into mesoporous silicas can be classified into three; 1) the adsorption of organic species onto mesoporous silicas, 2) grafting of mesopore surface with organosilanes, and 3) the use of organosilanes bearing covalently attached functional units as an inorganic source for the syntheses.[32] For thin film samples, which are relatively fragile compared with powder samples, the adsorption of cationic dyes into mesoporous silicas is attractive to construct functional silica-dye nanomaterials. Therefore, there is a demand for mesoporous silica films with controllable cation exchange capacity and acidic properties. The incorporation of aluminum into mesoporous silicas is a possible solution for this purpose.

Recently, we reported the successful synthesis of aluminum containing mesoporous silica films by a rapid solvent evaporation method.[30,31] The resulting films have been utilized as immobilizing media of a cationic azobenzene derivative, *p*-(ω-dimethylhydroxyethylammonioethoxy)azobenzene (hereafter abbreviated as AZ^+) bromide. Because the aluminum-containing mesoporous silica films are transparent and retain the mesostructure even after the adsorption of AZ^+, the adsorption of various cationic species onto the aluminum-containing mesoporous silica films is worth investigating. In this paper, we report the adsorption of methylene blue (MB) onto the aluminum-containing mesoporous silica films. The adsorption of MB onto various solid surfaces has been investigated previous-

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ly in order to probe the surface chemistry as well as to construct functional materials. We have already reported that MB was effectively adsorbed onto siliceous mesoporous silica films from a solution, in contrast to the case for AZ^+ which is not adsorbed onto siliceous mesoporous silica films.[31] Thus, the adsorption of cationic dyes onto mesoporous materials is not so simple and the interactions of mesopore surface and cationic dyes are worth investigating further. Since the visible absorption spectra of MB change depending on its environment, the states (interactions with surface and intermolecular interactions) of adsorbed MB can be discussed in addition to quantitative evaluation of cation exchangeable sites. The effect of the added aluminum on the adsorption characteristics of MB is further examined in the present study.

Experimental

Materials. Tetraethoxysilane (abbreviated as TEOS), aluminum tri(*s*-butoxide) (abbreviated as ATSB), and trimethyloctadecylammonium chloride (abbreviated as C18TAC) were obtained from Tokyo Kasei Industries Co. and used without further purification. Ethanol, acetonitrile, and hydrochloric acid are reagent grade, obtained from Tokyo Kasei Industries Co. Methylene blue (MB) was purchased from Tokyo Kasei Industries Co. and used as received.

Sample Preparation. Aluminum-containing mesoporous silica films were synthesized by a rapid solvent evaporation method as described previously.[30,31] A typical synthetic procedure for aluminum-containing silica-surfactant mesostructured materials is as follows: TEOS, ethanol, water and HCl (at the molar ratio of 1:4:1.2:0.006) were mixed at 50 °C for 10 min with magnetic stirring. To this solution was added ATSB and the mixture was allowed to react for another 10 min at 50 °C. Finally, C18TAC and aqueous HCl (pH = 2) were added and the mixture was allowed to react for 2 h at room temperature. The resulting solution was spin coated on a substrate and calcined in air at 350 °C for 6 h to prepare mesoporous silica films. The ATSB/TEOS ratio (molar ratio) was varied at 0.01, 0.02, 0.03, 0.04, and 0.05. Siliceous mesoporous silica film was also prepared by the above mentioned procedure.

The adsorption of MB was conducted by immersing the calcined films into an acetonitrile solution of MB at room temperature for 24 h. After the reaction, the films were washed with acetonitrile.

Characterization. X-ray diffraction patterns were obtained on a Mac Science, M03XHF[22] diffractometer using Mn filtered Fe $K\alpha$ radiation operated at 40 kV and 20 mA. Visible absorption spectra were recorded on a Shimadzu UV-2500PC spectrophotometer. Nitrogen adsorption isotherms of calcined films were measured at 77 K on a Bell Sorp TCV (Bell Japan Inc.). For the nitrogen adsorption measurements, films were prepared on a cover glass with the thickness of submicrometer. Prior to the measurement, the films were degassed under vacuum at 100 °C for 2 h.

Results and Discussion

By spin coating the precursor solution, we could form transparent thin films with the thickness of a few hundreds of nm formed. A single diffraction peak indicative of the formation of surfactant templated mesostructures was observed in the X-ray diffraction pattern of each sample, though the diffraction peak became broad with the increase in the loaded Al amount, as shown in Fig. 1. The transparency of the films was retained after the calcination. The X-ray diffraction patterns of the calcined films are shown in Fig. 2. The *d* values decreased upon calcination, suggesting the shrinkage of the, silica walls. The aluminum contents affected the regularity of the pore arrangements as shown by the broadening of the X-ray diffraction patterns (Figs. 1d–f and Figs. 2d–f). Similar observations have been reported previously for aluminum-containing mesoporous silica powders.[33–35]

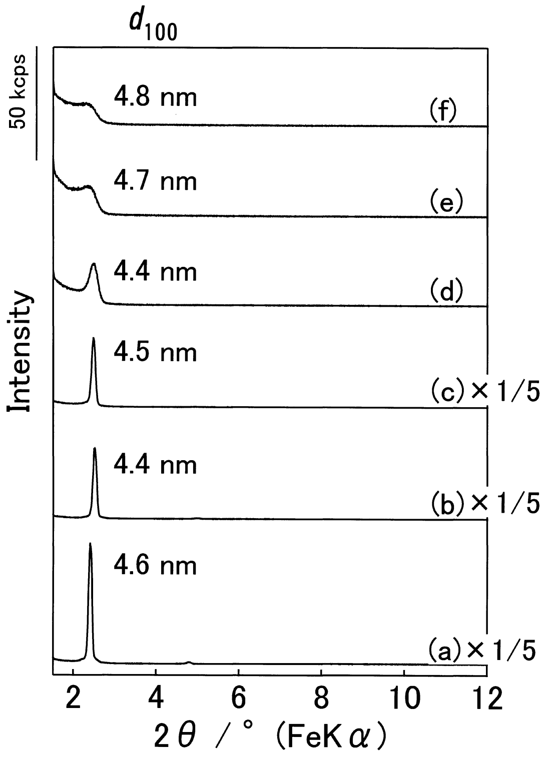

Fig. 1. X-ray diffraction patterns of the as synthesized films with the Al/Si = 0 (a), 0.01 (b), 0.02 (c), 0.03 (d), 0.04 (e), and 0.05 (f).

The nitrogen adsorption isotherms of the calcined films are type IV irrespective of the Al contents, showing that the films are mesoporous. The average pore sizes were derived from the isotherms by BJH method[36] to be 3.2, 3.0, 2.7, 2.7, 2.6, and 2.5 nm for the films with Al/Si = 0, 0.01, 0.02, 0.03, 0.04, and 0.05, respectively, confirming the formation of aluminum-containing mesoporous silica films. The pore sizes and the tendency to smaller pore size with the increase in the aluminum content are in accordance with those reported previously,[30,31] though the reason is not clear at present. The TEM images of the products also showed the presence of regularly sized mesopores. Note that the pore size is large enough to accommodate MB.

The adsorption of MB onto mesoporous silica films from solution takes place at room temperature to give colored films. The X-ray diffraction patterns of the films did not change by the reaction with MB, showing that the mesostructures were retained after the adsorption of MB. The visible absorption spectra of the MB adsorbed films are shown in Fig. 3. The absorption bands ascribable to MB (at 660 nm with a shoulder at 610 nm) appeared in the spectra and the absorbance increased

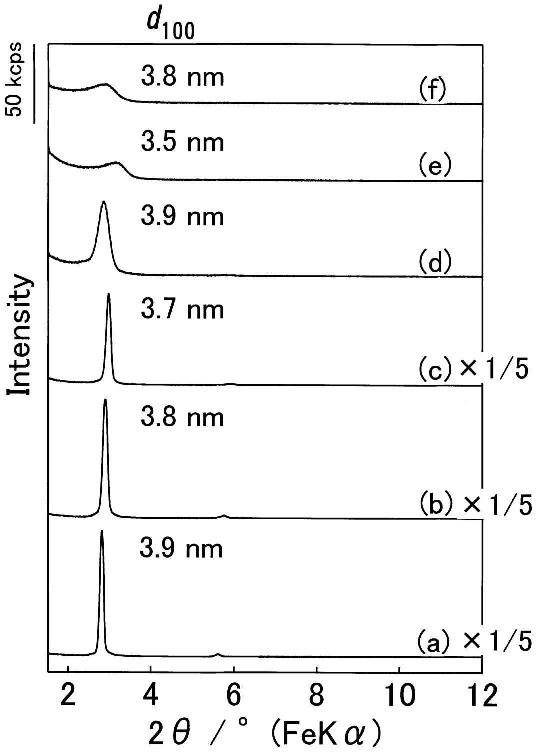

Fig. 2. X-ray diffraction patterns of the calcined films with the Al/Si = 0 (a), 0.01 (b), 0.02 (c), 0.03 (d), 0.04 (e), and 0.05 (f).

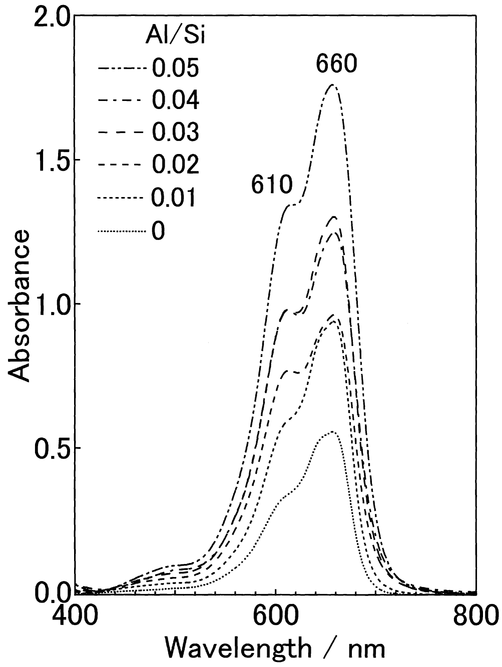

Fig. 3. Visible absorption spectra of the MB adsorbed films.

with the increase in the Al-content of the films. There is a general tendency to find increased absorbance at 660 nm due to monomeric MB with the increase in the Al-content of the films, as shown in Fig. 4. This relationship suggests that Al atoms substituted the framework Si to generate negatively charged sites for the MB adsorption. The deviation from the linear relationship shown in Fig. 4 was thought to be due to the existence of dimer and other aggregates. The variation of film thickness may also be important. Assuming that the molar absorption coefficient of the MB adsorbed in the mesoporous silica is the same as that of MB in dilute acetonitrile solutions and that the film thickness is 0.5 mm, we can determine the concentrations of the MB in the films to be 0.36, 0.26, 0.27, 0.20, 0.19, and 0.11 mol/L for the films with the Al/Si ratios of 0.05, 0.04, 0.03, 0.02, 0.01, and 0, respectively. It is worth noting as a merit of the present host-guest system that such high concentrations of MB without aggregation cannot be achieved in any solvents.

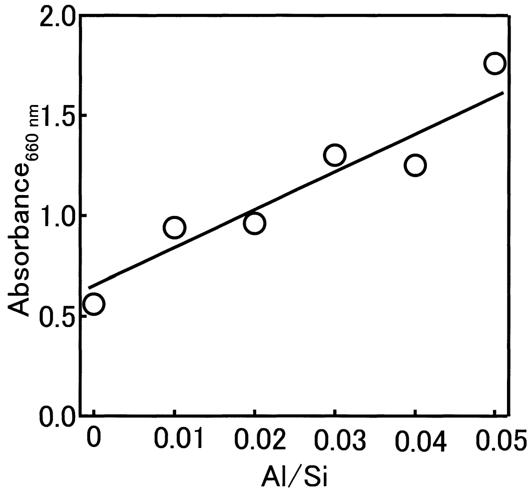

Fig. 4. Relationship between the Al-content of the films and the absorbance of MB monomer.

In our previous paper, we reported that cationic dyes, MB, 1,1′-diethyl-2,2′-cyanine, and tetrakis(*N*-methyl-4-pyridiniumyl)porphyrin, are adsorbed effectively on the siliceous mesoporous silica films.[18] On the contrary, the adsorption of AZ^+ occurred only on the aluminum-containing mesoporous silica films.[30,31] In the present system, MB was adsorbed on siliceous mesoporous silica films, confirming the previous report. The amounts of adsorbed MB increased after the incorporation of Al into the films. There was also a linear relationship between the Al content and the amount of adsorbed AZ^+ and the amounts were equivalent to the added Al content. On the other hand, ca. 20% of the added Al contributed to the increase in the adsorbed MB amount. It was thought that there are different interactions between the mesopore surface and MB: interactions of MB with siloxane or silanol surface and those with negatively charged sites generated by the isomorphous substitution of framework Si with the added Al. The difference in the molecular structures between MB and AZ^+ affected the quantitative difference in the adsorption capability. MB possesses three basic functional groups which can interact with the mesopore surface. The surfactant-templated mesoporous silicas possess unusually high surface area and porosity, so that the adsorption was not limited by the space but by the population of the sites to be interacted with MB on the mesopore. For the siliceous mesoporous silica films, the adsorbed MB did not fill the mesopores thoroughly, as suggested by the adsorbed MB amount determined by the absorbance.

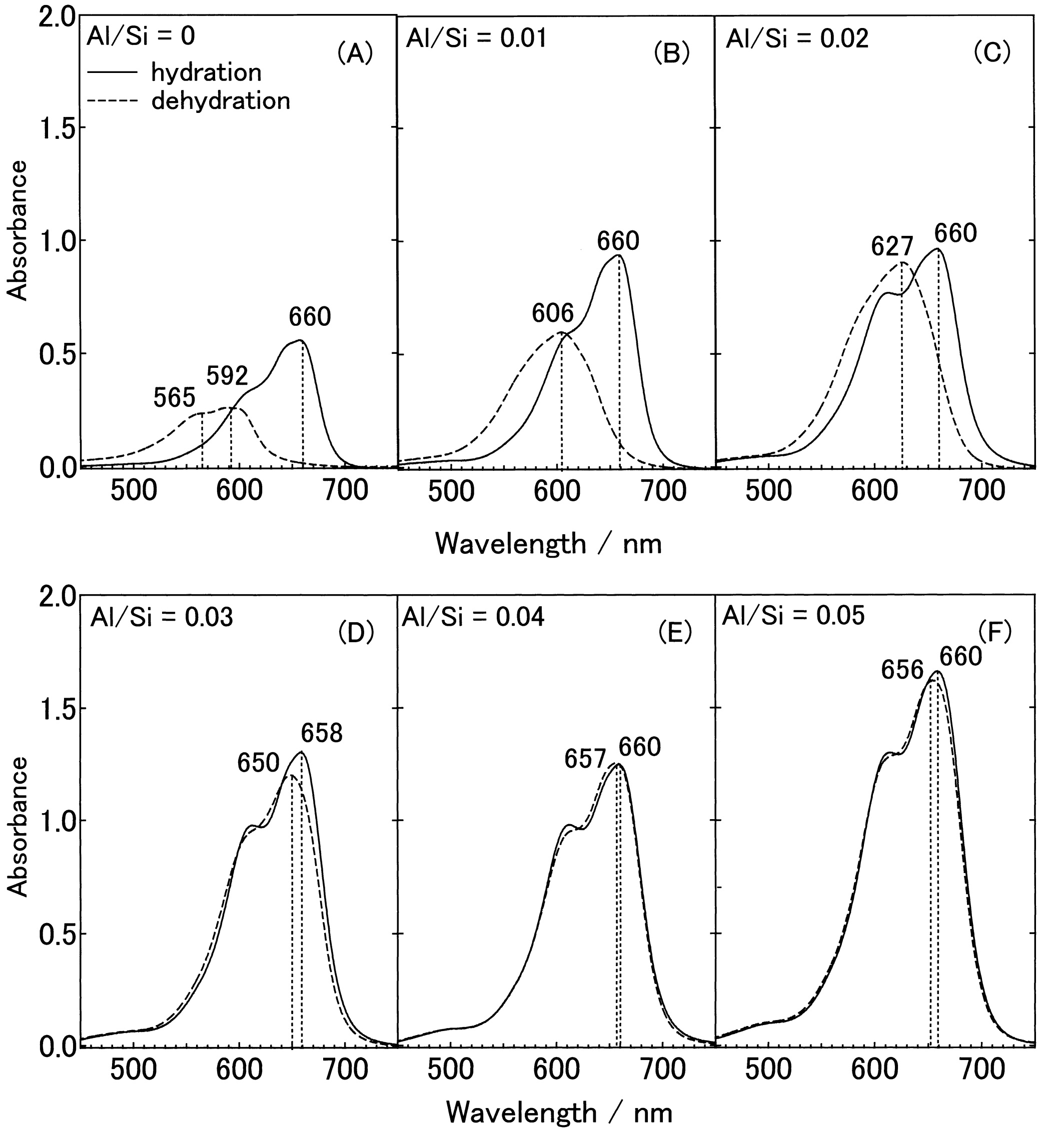

Fig. 5. The change in the absorption spectra of the MB adsorbed films upon drying. Solid and broken lines represent spectra before and after drying, respectively. Spectra observed for the films with Al/Si = 0 (A), Al/Si = 0.01 (B), Al/Si = 0.02 (C), Al/Si = 0.03 (D), Al/Si = 0.04 (E), and Al/Si = 0.05 (F).

In acidic environments, the dicationic form of MB predominates to give an absorption band at around 740 nm.[37,38] Such absorption bands have been observed when MB was adsorbed on solid acids such as Nafion films[37] and montmorillonite clays.[38] In the present system, the absorption band ascribable to the dicationic form of MB was absent, indicating that the acidity of the mesopore surface is not strong. The weak acidity has been discussed previously for the aluminum-containing mesoporous silica powders by means of various experimental techniques such as temperature programmed desorption of ammonia,[39] and the conclusions are consistent with the present observation.

The absorption spectra changed when the samples were dried at 100 °C, as shown in Fig. 5. This reflects the change in the states of the adsorbed MB. When siliceous films containing MB (Al/Si = 0) were dehydrated, the spectral feature dramatically changed to give the blue-shifted absorption bands with the maxima at 565 and 592 nm. The absorption bands at 565 and 592 nm are ascribable to trimer and higher aggregates of MB based on the previous papers.[37,38] During the dehydration, the adsorbed MB monomer diffused and aggregated in the mesopore. The pore size of the present film is large enough for MB to form aggregates.

On the other hand, the spectral changes are not so apparent when the aluminum-containing mesoporous silica films were dehydrated. The absorption bands ascribable to the trimer and higher aggregates were not observed and the monomer bands were dominant in the spectra of the films (Al/Si = 0.03, 0.04, and 0.05) even after the dehydration. It was thought that the negatively charged sites formed by the addition of Al distribute on the mesopore surface. The interactions of MB and the negative sites are strong compared with those with the mesopore surface of a siliceous film so that MB monomer was held on the surface to prevent aggregation. For the Al-containing mesoporous silica films with lower Al-contents (Al/Si = 0.01 and 0.02), the spectral change upon dehydration is complicated.

The absorption bands were shifted to shorter wavelength regions (with the absorption maxima at 606 and 627 nm for Al/Si = 0.01 and 0.02, respectively), although the assignments of the bands are difficult at the present stage.

It was reported that the absorption spectrum of MB in Nafion films changes by hydration.[37] The change was considered to be a result of different states of hydration of the anionic sulfonic groups which would alter the interactions with MB. In our separate study on the photoluminescence of tris(2,2′-bipyridine)ruthenium(II) complex on a mesoporous silica powder (C18-FSM), we have found that the luminescence intensity changed dramatically and reversibly depending on the water content.[40,41] It was thought that the aggregation of the complex on the mesopore surface was responsible for the change in the luminescence intensity. This means that the adsorbed complex cations can diffuse on the mesopores. In the present system, the aggregation of MB was shown by the change in the absorption bands.

As mentioned above, the adsorption behavior varies depending on the surface chemistry of the mesopores as well as the adsorbed guest species. In addition, the adsorbed states of the dyes varied depending on the host–guest systems as well as the co-adsorbed species. These observations suggest the difficulty and versatility of the materials design from host–guest complexation of mesoporous silicas. If compared with other host–guest systems, such as inclusion compounds of inorganic crystalline framework hosts and cyclodextrins, the experimental data are limited. Thus, the host–guest complexation from mesoporous silicas is worth investigating to understand the nature of the mesoporous silicas as well as to apply them as advanced materials.

Conclusions

Aluminum-containing mesoporous silica films were synthesized by rapid solvent evaporation method. Methylene blue was adsorbed effectively on the mesoporous silica films from solutions. The adsorbed amount increased with the increase in the aluminum content of the films, indicating that the added aluminum generated adsorption sites (probably acidic sites) for methylene blue adsorption. The mesopore surface is not strongly acidic since the protonation of methylene blue did not occur. Methylene blue exists as monomers in the mesopores and the dehydration of the films resulted in the aggregation of the dye in the mesopores.

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