Aluminium-containing mesoporous silica films as nano-vessels for organic photochemical reactions

Makoto Ogawa,*[ab] Kazuyuki Kuroda[cd] and Jun-ichi Mori[c]

[a] *Department of Earth Sciences, Waseda University, Nishiwaseda 1-6-1, Shinjuku-ku, Tokyo 169-8050, Japan. E-mail: makoto@mn.waseda.ac.jp*
[b] *PRESTO, Japan Science and Technology Corporation, Japan*
[c] *Department of Applied Chemistry, Waseda University, Ohkubo 3-4-1, Shinjuku-ku, Tokyo 169-8555, Japan*
[d] *Kagami Memorial Laboratory for Materials Science and Technology, Waseda University, Nishiwaseda 2-8-26, Shinjuku-ku, Tokyo 169-0051, Japan*

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The adsorption of a cationic azobenzene derivative into both siliceous and aluminium containing mesoporous silica films has been investigated; photoisomerization was found to occur in the temperature range 80–300 K and the mesoporous aluminium containing silica films were proved to be useful reaction media to immobilize organic photochromic species.

Mesoporous materials prepared by supramolecular templating approaches can accommodate guest species in their pores to form host–guest complexes and the resulting nanocomposites may exhibit useful functions in the areas of catalysis, adsorption and sensing.[1] Here we report the synthesis of the aluminium containing mesoporous silica films for the first time and applied these as nano-reactors for organic photochemical reactions. Photochemistry in constrained media is a growing new field which yields a wide variety of useful applications including sensitive optical media, reaction pathways for controlled photochemical reactions, and molecular devices for optics.[3] For such applications, mesoporous silica films possess attractive features such as large surface areas and porosity, controllable pore sizes, reactive pore surfaces, and stability over a wide temperature range.

In the present study, the introduction of a cationic azobenzene into the mesoporous silica films was conducted using *p*-(ω-dimethylhydroxyethylammonioethoxy)azobenzene bromide (AZ) as the guest species. Photochemical reactions of azobenzenes are sensitive to the microenvironment and so can be employed as photoreactive probes to estimate microenvironments (free volume and rigidity), to which conventional characterization techniques do not have an access.[4] Moreover, geometrical changes of azobenzenes have been utilized as a trigger to design photoresponsive supramolecular systems.[5,6] Accordingly, the photochemistry of azobenzenes in mesopores is worth investigating from the viewpoints of probing mesopores as well as constructing photofunctional materials.

Aluminium-containing mesoporous silica films were synthesized by the rapid solvent evaporation method which we have developed.[7] This method is promising for the preparation of silica-surfactant mesostructured materials in a controlled morphology,[8,9] since the reaction is very simple and the resulting films are highly transparent and homogeneous. Aluminium tris(*sec*-butoxide) (ATSB) was used as the aluminium source and co-solidification with silica was conducted by the reported synthesis method for aluminosilica xerogels[10] with slight modification. A typical synthetic procedure for the transparent thin films of aluminium-containing silica-surfactant mesostructured materials is as follows: silicon tetraethoxide (TEOS), ethanol, water and HCl (molar ratio of 1 : 4 : 1.2 : 0.006) were mixed at 60 °C for 10 min with magnetic stirring. ASTB was then added and the mixture allowed to react for a further 10 min at 60 °C. Then, an aqueous solution of octadecyltrimethylammonium chloride was added and the mixture allowed to react for a further 2 h at room temperature. The resulting solution was spin coated on a substrate and calcined in air at 300 °C for 18 h to prepare mesoporous silica films; ASTB/TEOS ratios were set at 0.05, 0.031, 0.025, 0.022 and 0.014.

SEM images of the film surfaces (data not shown) indicate that the films are continuous and crack free when the ASTB/TEOS ratios were 0.031, 0.025, 0.022 and 0.014. When the ASTB/TEOS ratio was increased to 0.05, a homogeneous solution cannot be obtained under the experimental conditions and the resulting film is slightly turbid. The X-ray diffraction patterns of the calcined films with different Al contents are shown in Fig. 1(a)–(c). Although the diffraction peaks broadened with an increase in the loaded Al amount, a single diffraction peak indicative of the surfactant templated mesostructures was observed for all the samples. Nitrogen adsorption isotherms of the calcined films on a glass substrate are of type IV indicating that the films are mesoporous. The average pore sizes as derived from the isotherms by the Horvath–Kawazoe method[11] were 3.2, 2.9 and 2.8 nm for the films with Al/Si = 0, 0.014 and 0.031, respectively.

For the introduction of AZ, the mesoporous silica films were immersed in an ethanol solution of AZ. The amount of AZ adsorbed onto the Al free film was very low even for extended reaction times or if a concentrated AZ solution was used. On the other hand, AZ was adsorbed effectively into the Al containing mesoporous silica films. It is thought that the partial substitution of Si by Al leads to successful introduction of AZ into the mesopores through electrostatic interactions between the dye and the negative charge at the substituted Al site. The UV–VIS absorption spectrum (Fig. 2) of the film (Al/Si = 0.0031) after the reaction with AZ showed an absorption band centered at 338

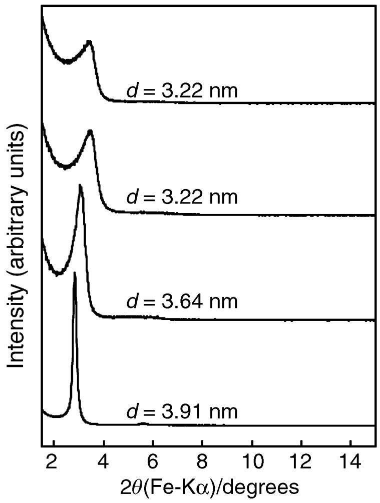

Fig. 1 X-Ray diffraction patterns of mesoporous silica films with Al/Si = 0 (a), 0.0014 (b) and 0.0031 (c); trace (d) is (c) after adsorption of AZ.

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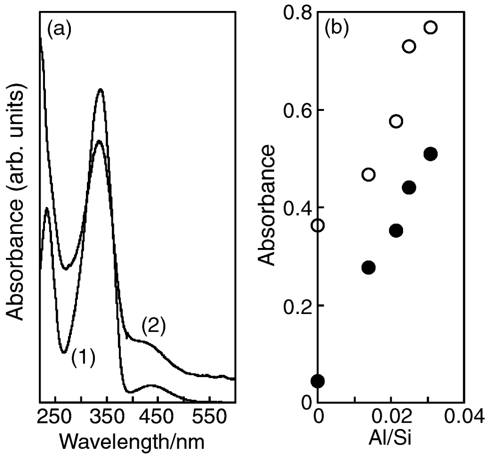

Fig. 2 (a) Absorption spectra of (1) 0.03 mmol L^{-1} AZ ethanol solution and (2) the AZ adsorbed mesoporous silica film (Al/Si = 0.0031). (b) The variation of the absorbance due to *trans*-AZ at 340 nm as a function of the Al/Si ratio. Open and filled circles represent samples before and after washing with ethanol.

nm, which is ascribable to the π–π* transition of *trans*-AZ. With an increase in the Al content, the absorbance due to *trans*-AZ increased as shown in the inset of Fig. 2. The absorbance of the films after washing with ethanol is also shown in Fig. 2(b). The absorbance due to *trans*-AZ was decreased by washing, indicating that weakly bound AZ was removed from the films. As seen in Fig. 2(b), the decrease in the absorbance is almost same irrespective of the amount of loaded Al, suggesting that there are two different adsorption sites for AZ; strongly acidic sites at the substituted Al and weakly acidic sites probably at the silanol groups. Intermolecular interactions between adsorbed AZ may also be a factor leading to differences in behavior of the adsorbed species.

The absorption maximum observed for the film (Al/Si = 0.0031) essentially matched that of a dilute (3 × 10^{-5} M) ethanol solution of the dye. Considering the fact that the absorption spectra of aggregated AZ molecules such as found in crystals or AZ adsorbed on a layered silicate[12] are quite different from that of the present system, it is clear that the AZ cations are adsorbed and dispersed as monomers on the surface of the mesoporous silica irrespective of the amount of loading. Assuming that the molar absorption coefficient of AZ adsorbed in the mesoporous silica is the same as that of AZ in a dilute ethanol solution and that the film thickness is 0.5 μm, the concentrations of the AZ in the films are determined to be 0.42, 0.37, 0.29 and 0.23 mol L^{-1} for the films with Al/Si ratios of 0.031, 0.025, 0.022 and 0.014, respectively. Such high concentrations of AZ cannot be achieved in any solvents due to solubility limitations. The AZ cations are thought to be distributed in the one-dimensional channels with a mean separation between adjacent AZ molecules of 1.7 nm at the maximum loading level (Al/Si = 0.031).

When the as-coated films were calcined at higher temperature (*i.e.* 450 °C), the capacity for the adsorption of AZ was dramatically decreased. This observation can be rationalized by the condensation of hydroxy groups on the mesopore surfaces as well as diffusion of the loaded Al into the silica walls from the pore surface. Since the films are thin (0.5 μm), oxidative decomposition of the template is facile when compared with surfactant occluded in the bulk samples. Thus, the mesoporous silica films with cation exchangeable sites on the pore surfaces are readily available by surfactant removal at relatively low temperature (300 °C).

The adsorbed AZ in the mesopores exhibits photochemical isomerization upon UV and visible light irradiation.[13] The reactions were monitored by the change in the absorbance of the *trans*-isomer of the AZ at 340 nm and a typical change in the absorption spectrum is shown in Fig. 3(a). The ratio of the *cis*-isomer formed by the UV irradiation at the photostationary state at room temperature was roughly estimated to be no less than *ca.* 90% from the absorbance change. It is known that the photoisomerization is affected by the free volume and the rigidity of the surroundings.[14–16] The van der Waals volume of azobenzene is 144 Å^3 and photoisomerization requires an extra 127 Å^3.[15] The pore size of the mesoporous silica films used in the present study is large enough for AZ to isomerize. The photochemical isomerization was measured in the temperature range 80–400 K and the temperature dependence of the yield of the photochemical reactions is shown in Fig. 3(b). Photochemical isomerization occurs even at 80 K, showing that the mesoporous silica films can be utilized as a nano-reaction vessel in a wide temperature range for organic photochemical reactions.

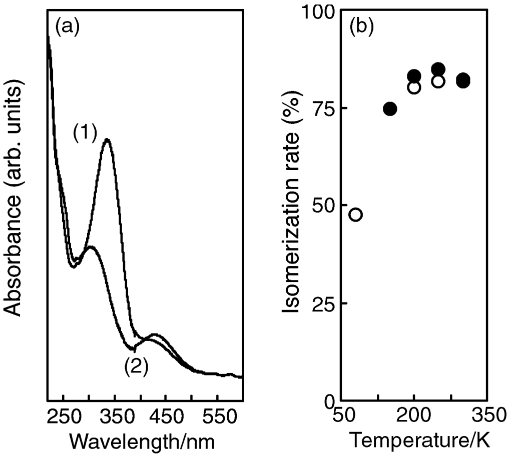

Fig. 3 (a) The change in the absorption spectrum of the AZ adsorbed mesoporous silica film (Al/Si = 0.0031) before (1) and after (2) UV irradiation. (b) The temperature dependence of the fraction of the photochemically formed *cis*-isomer at the photostationary states for the AZ adsorbed mesoporous silica film (Al/Si = 0.0031). Open and filled circles represent the values obtained on cooling and heating, respectively.

Notes and references

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