Original Research Paper

J. Jpn. Soc. Colour Mater., 85 [11], 439–448 (2012)

Ultraviolet Absorption Capabilities of Iron-Containing Mesoporous Silicas Synthesized by Various Methods

Amata CHAIKRIANGKRAI*, Yuka TAKESHITA* and Masashi SHIBATA*[†]

*School of Bioscience and Biotechnology, Tokyo University of Technology, 1404-1 Katakuramachi, Hachioji City, Tokyo 192-0982, Japan

[†]Corresponding Author, E-mail: mshibata@bs.teu.ac.jp

(Received April 9, 2012; Accepted September 24, 2012)

Abstract

Ultraviolet absorption capabilities of Fe-containing mesoporous silicas (Fe-MPSs) synthesized using different Fe sources, template removal methods, and types of Fe-MPSs were studied. Further, the potential of Fe-MPSs as ultraviolet protecting agents was considered by UV transmittance of thin films of the samples, their color and also photo-catalytic activities. Calcined MCM-41 type Fe-MPS which is synthesized via iron (III) acetylacetonate showed the best ultraviolet absorption capability but is slightly brown when Fe/Si mole ratio ≥ 0.02 . Contrastingly, both MCM-41 and HMS type Fe-MPS using Fe(acac)₃ as the iron source and removing the template by solvent extraction yielded white powder even though ultraviolet absorption was relatively low. Furthermore, the UV transmittances of thin films of aqueous slurries of the suggested calcined Fe-MPS (Fe/Si mole ratio = 0.02) were equal to that of aqueous slurry of silica surface treated TiO₂. In addition, there was no photocatalytic activity detected in Fe-MPSs synthesized by both suggested methods. These results indicate that Fe-MPSs synthesized by the conditions suggested in this study have the potential for use as new ultraviolet protecting agents.

Key-words: Fe-containing mesoporous silica, Ultraviolet protecting agent, Ultraviolet absorption capability, Photo-catalytic activity

1. Introduction

Ultraviolet radiation (UVR) is one of the causes of skin problems such as sunburn, hyper-pigmentation, and photo-aging^{1,2,4}. It is known that exposure to UVB can cause acute skin erythema and sunburn. On the other hand, UVA can penetrate relatively deep skin layers and may cause DNA damage as well as skin cancer³. Therefore, many specialists recommend applying sunscreen to protect the skin against the harmful effects of UVR^{2,3,25}.

There are two types of sunscreen agents-organic and inorganic. Organic sunscreen agents such as methoxy cinnamate ester and oxybenzone are widely used in sunscreen products. However, there are some concerns about allergic reactions to these agents⁵. On the other hand, inorganic sunscreen agents such as TiO₂ and ZnO are becoming increasingly popular because of their favorable protection against both UVA and UVB and relative safety. However, inorganic sunscreen agents generally tend to form visible white films on the skin, thus leading to an unnatural appearance⁶. Furthermore, their particle surfaces are reactive, especially TiO₂, which has strong photo-catalytic properties^{7,8}. Thus far, there have been many attempts to increase their transparency by reducing the particle size⁹ and to reduce the surface reactivity by coating their surfaces with inert substances¹⁰. Nevertheless, difficulties remain in that it is difficult to perfectly coat the particle surface,

and an uncoated reactive surface can consequently lead to a shortening of the product shelf life^{7,8,10}.

In order to overcome those drawbacks, a new inorganic sunscreen material is desired that does not show photo-catalytic activity and does not form a visible film or cause allergic reactions when applied on the skin. Moreover, in some specific applications, colorless sunscreens are required, for example, application into lip glosses or lip cream for which the product colors will be changed if colored agents are used. Mesoporous silica (MPS) is a material formed by a silica framework with pores ranging in sizes from 2 to 50 nm, and it has been researched in various fields such as catalytic chemistry and adsorptive separation because of its high surface area and well-ordered controllable pores. In addition, various heterometal ions can be incorporated into the MPS framework in order to vary the chemical and physical properties. There have been many studies on metal-incorporated MPSs such as Al¹⁶), Fe¹³⁻¹⁵), Ti¹⁷), and Zn-containing MPSs¹⁴). It is well known that for the transition metal oxide species, the energy of the absorption edge corresponds to the band gap energy (Eg), and the Eg generally changes with the local coordination structure of the species³⁶. In 1984, the data for iron complexes with four, five, and six coordination were reported by Roe *et al*³⁵). It was reported that the Eg (I) of the Fe oxide is determined by the local coordination of iron and decreases in the following sequence:

I (tetrahedral) > I (square pyramidal) > (octahedral)³⁵.

Presently, many researchers have reported that Fe-containing MPS can absorb ultraviolet radiation and exhibit distinct peaks at 220 and 260 nm, which are related to electron transfer from the ligands to the t_{2g} and e_g orbitals¹²⁻¹⁶. However, some Fe atoms are not incorporated into the Si network and are oxidized to Fe_2O_3 outside the framework. These extra-framework Fe show visible photo-absorption properties causing the color of the obtained powder to be light brown^{15,16}. This phenomenon is caused by the difference between band gap energies (E_g) in the tetrahedral form and the octahedral form of Fe which are about 4.68 eV and 2.10 eV respectively¹³⁻¹⁶.

Generally, coordination of iron (III) oxide is in the octahedral form and it absorbs visible region light showing dark red to brown color. Contrastingly, when Fe is incorporated into silica framework of MPS, the coordination of Fe turns to the tetrahedral form (FeO_4^-), and its photo-absorption property shifts from the visible region (400-800 nm) to the ultraviolet region (200-400 nm). These phenomena suggest the possibility of using Fe-containing MPS as a UV protecting agent with ultraviolet absorption capability. However, most of the studies on the synthesis of Fe-MPS have focused on using Fe-MPS as a catalyst for redox reactions^{17-19,21,22}; there is insufficient research presently on which synthesis method of Fe-MPS and which type of MPS are preferable when aiming to use them as UV protecting agents.

In our previous work, we reported that calcined MCM-41 type Fe-MPS which is synthesized via iron (III) acetylacetonate showed the best ultraviolet absorption capability²⁰. However, in the present work, we report the ultraviolet absorption capabilities of Fe-MPS based on other synthesis conditions. The variables in synthesis conditions were as follows: multiple Fe sources, template removal methods, and types of mesoporous silicas. Furthermore, we estimate practical uses of synthesized samples by measuring UV transmittances of thin films of aqueous slurry samples. Furthermore their photo-catalytic activities were also evaluated.

The ideal properties of UV protecting Fe-MPSs are considered to be as follows

- (1) High surface area with uniform mesopore resulting in good dispersibility in various media
- (2) Based on UV-Vis diffuse reflectance spectra, high UV absorption (intra-framework Fe) with no visible absorption (extra-framework Fe)
- (3) Possessing not only high UV absorption based on (2), but also no UV transmittance of the thin films of the samples
- (4) No photo-catalytic activity of the sample (as UV absorbing agents tend to be photo-catalysts)

2. Experimental

2.1 Synthesis of iron-containing material

All the materials in this study, except the specified ones, were analytical grade, obtained from Wako Chemical, and used as received.

2.1.1 Synthesis of iron-containing Mobil crystalline material-41 and iron and aluminium-containing Mobil crystalline material-41(Fe-MCM-41, Fe/Al-MCM-41)

Hexadecyltrimethyl ammonium bromide (C16TMABr, 2.28 g) was dissolved in 44.3 g of purified water and stirred at 313 K for 1 h (solution A). Tetraethyl orthosilicate (TEOS, 10.29 g) was mixed with an Fe source, iron (III) acetylacetonate ($Fe(acac)_3$, Kanto Chemical Co., Fe/Si molar ratio = 0.01, 0.02, or 0.05), and a sufficient amount of ethanol was added (solution B). When iron (III) nitrate, ($Fe(NO_3)_3 \cdot 9H_2O$), was used as an Fe source, it was dissolved in solution A instead of solution B. Next, 0.58 g of NaOH in 6.3 g of purified water and solution B were alternately added dropwise to solution A within 15 min while the mixture was being vigorously stirred at room temperature. After stirring for additional 2 h, the temperature was increased to 413 K and the mixture was kept static for 48 h. Then, the product was recovered, washed until pH was ca. 8, and dried overnight at 333 K under reduced pressure.

To remove the template from Fe-MCM-41, one of three procedures was selected. One method was the calcination of Fe-MCM-41 at 873 K for 6 h by air blasting. The second method was solvent extraction by stirring 4 g of the as-synthesized product with 300 mL of ethanol and 2 mL of 2 M HCl for 6 h. This process was repeated twice. The third method was a combination of the first two methods, wherein solvent extracted Fe-MCM-41 was calcined for 6 h at 873 K. For Fe/Al-MCM-41, we mixed 0.2 g of Al-MCM-41 synthesized by the method reported in our previous work²³ with 4 mL of ethanolic solution of $Fe(acac)_3$ (Fe/Si Ratio = 0.02) and vigorously stirred at 323 K for 1h. Then, the product was recovered, dried overnight at 333 K under reduced pressure and calcined at 873 K for 6 h by air blasting.

2.1.2 Synthesis of iron-containing hexagonal mesoporous silica (Fe-HMS)

Dodecylamine (DDA, 0.91 g) was dissolved in 7.5 g of ethanol; after adding 45 g of purified water, the solution was vigorously stirred at room temperature for 2 h. TEOS (4.64 g) was mixed with a suitable amount of $Fe(acac)_3$ (Fe/Si molar ratio = 0.01, 0.02, or 0.05) and a sufficient amount of ethanol. Next, the Fe- and Si-containing solution was added dropwise within 15 min to the previously prepared surfactant solution while the mixture was stirred vigorously. When iron (III) nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) was used as the Fe source, it was

prepared separately from the Si source, and the Fe and Si sources were alternately added dropwise to the surfactant solution. After sitting for 24 h at room temperature, the product was recovered, washed three times with 500 mL of ion-exchanged water, and then dried overnight at 333 K under reduced pressure. Finally, for template removal, some of the product was calcined at 873 K for 6 h by air blasting. On the other hand, another part of the product was subjected to solvent extraction, where 1.7 g of the as-synthesized product was stirred in 50 mL of ethanol at 323 K for 1 h; this process was repeated three times. The remaining amount of product was subjected to a combination of these two methods, wherein solvent-extracted Fe-HMS was calcined for 6 h at 873 K.

2.1.3 Synthesis of iron-containing Santa Barbara amorphous-15 (Fe-SBA-15)

Poly(ethylene glycol)₂₀-poly(propylene glycol)₇₀-poly(ethylene glycol)₂₀ (P123, 2 g), which was used as a template, was dissolved in 70 mL of HCl solution with pH = 4 (solution A) and stirred at 313 K for 2 h. An appropriate amount of Fe(NO₃)₃·9H₂O (Fe/Si molar ratio = 0.01, 0.02, or 0.05) was dissolved in 5 mL of purified water (solution B). TEOS (4.5 g) and solution B were alternately added dropwise within 15 min to solution A, and then the mixture was continuously stirred at 313 K for additional 24 h. After that, the temperature was increased to 373 K and the mixture was kept static for 24 h. The product was recovered, washed until pH was c.a. 7 with ion-exchanged water, and dried overnight at 333 K under reduced pressure. Lastly, for template removal, the product was subjected to the three methods. First, some of the Fe-SBA-15 was calcined at 873 K for 6 h by air blasting. Second, some of the product was subjected to solvent extraction, during which 0.5 g of the as-synthesized product was refluxed for 6 h in 50 g of a mixture with a molar ratio of EtOH:HCl:H₂O = 192:3:5. In the third method, a combination of these two methods was used; solvent-extracted Fe-SBA-15 was calcined for 6 h at 873 K.

2.1.4 Synthesis of iron-containing silica gel (Fe-silica)

Tetraethyl orthosilicate (TEOS, 10.29 g) was mixed with iron (III) acetylacetonate (Fe(acac)₃, Kanto Chemical Co., Fe/Si molar ratio = 0.02) and a sufficient amount of ethanol to yield solution A. Then, solution A was added dropwise within 15 min to aqueous NaOH, which was prepared by dissolving 0.58 g of NaOH in 45 g of purified water. Next, the mixture was stirred vigorously at room temperature for 2 h and then kept static at 413 K for 48 h. The product was recovered, washed until pH was ca. 8, and dried overnight at 333 K under reduced pressure. Finally, it was calcined at 873 K for 6 h by air blasting.

2.2 Characterizations

Nitrogen sorption measurements were performed using a Shimadzu Tristar 3000 micrometrics analyzer. Surface area

was calculated by the Brunner-Emmett-Teller (BET) method. Pore size and pore volume were determined by the Barrett-Joyner-Halenda (BJH) method using the peak of the desorption branch. Scanning electron microscopy (SEM) images were taken with a JEOL JSM-6060LV microscope. Chemical analysis was performed by Energy-dispersive X-ray spectroscopy (EDS) equipped with SEM, which was calibrated with standard samples consisting of silica and iron oxide. Ultraviolet-visible diffuse reflectance spectra were measured using a Jasco V-650 spectrophotometer equipped with an integrating sphere (ISV-722) and data were converted to absorbance spectra by using Beer's law ($A = 2 - \log_{10} \%T$) and using a $\pm 1\%$ flatness degree white plate as a baseline. Ultraviolet absorption capability of samples are estimated by using absorbance ratios of area under the curve (AUC) of UV region (200-400 nm) to AUC of visible region (400-800 nm), A_{UV}/A_{VIS} ratio.

The UV transmittance (290-400 nm) of thin films of samples was measured in order to preliminarily estimate the UV protecting abilities. First, the sample was dispersed in purified water (with a maximum dispersible amount) using a mixer (Vortex Genie 2). Then, the sample was placed on a quartz glass plate and covered with a glass slide in order to create a uniform thickness of 23.6 μm . The film of TiO₂ was prepared in the same way using silica surface treated nanoparticle titanium dioxide ($d=0.01 \mu\text{m}$, Ishihara Sangyo Kaisha, Ltd.). The UV transmittance (290-400 nm) of the obtained powder film was measured on JASCO V-650, and the SPF and PA values were simply estimated by using the SPF and PA value calculation program, JASCO VWSP-787. The equations for SPF and PA value are as follows.

$$\text{SPF} = \frac{\sum_{290}^{400} E(\lambda) \cdot R(\lambda)}{\sum_{290}^{400} T(\lambda) \cdot E(\lambda) \cdot R(\lambda)}, \quad \text{PA} = \frac{\sum_{320}^{400} M(\lambda) \cdot E(\lambda)}{\sum_{320}^{400} T(\lambda) \cdot M(\lambda) \cdot E(\lambda)}$$

$E(\lambda)$ = Distribution of light source energy based on Australia/New Zealand (AS/NZ) standard 2604:1998

$R(\lambda)$ = Spectrum of CIE reference erythema action

$T(\lambda)$ = Transmittance spectrum (290-400 nm)

$M(\lambda)$ = Spectrum of Minimum instantaneously continuous tanning action (value=1.0 for this study)

Finally, photo-catalytic activities of the product were estimated by photo-degradation of an azo dye solution (F&D red no.6, Daito Kasei Kogyo Co.). 0.01 g of anatase TiO₂ powder (as a standard of photo-catalyst) or 0.025 g of the product was dispersed in 3.0 g of the dye solution (maximum absorbance at 493 nm was around 3) and transferred to a glass petri dish ($\Phi = 3 \text{ cm}$). Then, the product was stirred under a UVA lamp (10-W Toshiba black light; $80 \mu\text{W}/\text{cm}^2$) while the reference was stirred in the dark. After 30 min, both the products were recovered and the absorbance values of each supernatant were measured. The photo-catalytic activity

was estimated by observing the absorbance change at 493 nm by UV irradiation.

3. Results and Discussion

3.1 Mesoporous structure and chemical analysis

N₂ sorption measurements (surface areas, pore volumes, and pore diameters) of all the samples (Table 1) were performed to confirm the formation of mesoporous structures. SEM images (Fig. 1) of some samples were also obtained. Generally, a sample with a high surface area (> 800 m²/g) and a uniform porous structure (pore size 2-50 nm) is characterized as a mesoporous material^{24,25}. We reported in our past work that MPSs with secondary sizes smaller than 5 μm showed preferable distribution profiles³². As shown in Table 1, the surface area of Fe-nonporous silica (sample no.21) was < 200 m²/g. In addition, the pore volume and pore diameter could not be measured, indicating that porous structure was not formed in the silica network. Meanwhile, the surface areas of most of the other samples (Fe-MPSs) were around 800-1000 m²/g, with pore diameters of around 2-3 nm (for Fe-MCM-41 and Fe-HMS) and around 7 nm (for Fe-SBA-15), except for sample nos. 7, 8, and 15. The surface areas of sample nos. 7, 8, and 15 were relatively low, but sharp pore size distribution peaks were observed, indicating that uniform

mesoporous structures were formed. On the basis of these values, it can be inferred that mesoporous structures were successfully synthesized. We propose that the excess Fe in sample nos. 7, 8, and 15 was oxidized to octahedral iron oxide at extra-framework sites on the meso-structured surfaces and inside some mesopores, resulting in the decrease in the surface

Fig. 1 SEM images of (a) Fe-MCM-41 (Fe/Si = 0.02) via Fe(acac)₃ (sample no.1), (b) Fe-MCM-41 (Fe/Si = 0.05) via Fe(acac)₃ (sample no.7), (c) Fe-HMS (Fe/Si = 0.01) via Fe(acac)₃ (sample no.12) and (d) Fe-SBA-15 (Fe/Si = 0.01) via Fe(NO₃)₃·9H₂O (sample no.19).

Table 1 Synthesis conditions, Chemical analysis and surface characterization of Fe containing materials.

Samples	Fe/Si mole ratio mixture	Fe/Si mole ratio product ^a	Type of carriers ^b	Fe sources ^c	Template removal methods	S _{BET} ^d (m ² /g)	Pore V ^e (cm ³ /g)	Pore D ^f (nm)
no.1	0.02	0.023	MCM-41	Fe (acac) ₃	calcination	960	0.87	2.83
no.2	0.02	0.025	MCM-41	Fe (NO ₃) ₃	calcination	904	0.78	2.92
no.3	0.02	0.011	MCM-41	Fe (acac) ₃	solvent ext.	943	0.90	3.03
no.4	0.02	0.011	MCM-41	Fe (acac) ₃	sol ext.+cal	953	0.73	2.97
no.5	0.01	0.007	MCM-41	Fe (acac) ₃	calcination	1038	1.00	3.20
no.6	0.01	0.004	MCM-41	Fe (acac) ₃	solvent ext.	1045	0.99	3.07
no.7	0.05	0.049	MCM-41	Fe (acac) ₃	calcination	385	0.27	2.67
no.8	0.05	0.029	MCM-41	Fe (acac) ₃	solvent ext.	561	0.43	2.75
no.9	0.02	0.027	HMS	Fe (acac) ₃	calcination	1218	0.88	2.37
no.10	0.02	0.011	HMS	Fe (NO ₃) ₃	calcination	1045	0.90	2.54
no.11	0.02	0.021	HMS	Fe (acac) ₃	solvent ext.	936	0.57	2.19
no.12	0.01	0.014	HMS	Fe (acac) ₃	calcination	1240	0.93	2.40
no.13	0.01	0.014	HMS	Fe (acac) ₃	solvent ext.	1163	0.81	2.34
no.14	0.05	0.046	HMS	Fe (acac) ₃	calcination	1126	0.59	2.19
no.15	0.05	0.045	HMS	Fe (acac) ₃	solvent ext.	756	0.73	2.14
no.16	0.02	—	SBA-15	Fe (acac) ₃	calcination	no reaction		
no.17	0.02	0.019	SBA-15	Fe (NO ₃) ₃	calcination	930	1.06	7.27
no.18	0.02	0.011	SBA-15	Fe (NO ₃) ₃	solvent ext.	920	0.80	7.53
no.19	0.01	0.004	SBA-15	Fe (NO ₃) ₃	calcination	923	0.92	7.60
no.20	0.05	0.042	SBA-15	Fe (NO ₃) ₃	calcination	893	0.96	6.09
no.21	0.02	0.022	NP silica	Fe (acac) ₃	calcination	<200	undetectable	

^a Fe/Si mole ratios measured by Energy Dispersive x-ray Spectroscopy equipped Scanning Electron Microscope (JEL6600L).

^b Types of carriers were referred by Mobil Crystalline Material 41 (MCM-41), Hexagonal Mesoporous Silica (HMS) and Santa Barbara Amorphous type material 15 (SBA-15).

^c Fe sources were referred by ferric nitrate nonahydrate (Fe (NO₃)₃) and ferric acetylacetonate (Fe (acac)₃).

^d Surface area data were calculated by the Brunner-Emmett-Teller (BET) method.

^{e,f} Pore diameters and volumes that were determined by Barrett-Joyner-Halenda (BJH) method using the peak of the desorption branch of the isotherm.

Table 2 UV absorption capabilities of Fe containing materials.

Samples	Fe/Si mole ratio		Type of carriers ^b	Fe sources ^c	Template removal methods	A _{UV} ^a	A _{vis} ^b	A _{UV} /A _{vis} ^c
	mixture	product ^a						
no.1	0.02	0.023	MCM-41	Fe (acac) ₃	calcination	0.9	0.6	3.45
no.2	0.02	0.025	MCM-41	Fe (NO ₃) ₃	calcination	0.9	0.3	1.91
no.3	0.02	0.011	MCM-41	Fe (acac) ₃	solvent ext.	0.7	0.1	2.77
no.5	0.01	0.007	MCM-41	Fe (acac) ₃	calcination	0.8	0.1	4.79
no.7	0.05	0.049	MCM-41	Fe (acac) ₃	calcination	1.0	0.4	2.58
no.9	0.02	0.027	HMS	Fe (acac) ₃	calcination	0.7	0.2	2.57
no.17	0.02	0.019	SBA-15	Fe (NO ₃) ₃	calcination	0.8	0.6	1.35

^a Peak Absorbance measured at UV region (200~400 nm).^b Peak Absorbance measured at Visible region (400~800 nm).^c Ratio of Peak Absorbance measured at UV region (200~400 nm) to Visible region (400~800 nm).

area. Moreover, the surface area of the Fe-MPS samples was found to change with the surfactant removal method used. With some exceptions, the surface areas of calcined samples were higher than those of solvent-extracted ones. Thus, it can be considered that calcination at 873 K for 6 h removed all the surfactants located in the pores, whereas solvent extraction could only remove some of the surfactants.

Next, the secondary structures of some Fe-MPS samples were observed by SEM with a magnification of up to 14,000 times. All the samples were round in shape, but the diameters varied according to the Fe/Si ratio. For sample nos.1 and 5, the particle sizes were around 1 μm (Fig. 1a), whereas that of sample no.7 was 0.3 μm (Fig. 1b), which was relatively small. Moreover, sizes varied according to type of MPS. Sample no.19 had a secondary particle size of around 2 μm (Fig. 1d), whereas sample no.12 had a size of around 1 μm but was more clustered (Fig. 1c). According to these results, it can be concluded that all the Fe-MPSs have mesoporous structures and their secondary shapes and sizes are of the preferred type.

3.2 Ultraviolet absorption capability

As stated earlier, it is known that the spectroscopic properties of Fe change with a change in its coordination form. Intra-framework Fe, which is in the tetrahedral form (FeO_4^-), absorbed ultraviolet radiation. On the other hand, extra-framework octahedral Fe absorbed visible light¹¹⁻¹⁶. Thus, we can preliminarily state the coordination form of Fe in Fe-MPS powder by observing the color of the synthesized powders. A totally white powder denotes the totally intra-network tetrahedral Fe, while a pale yellow to light brown (the exact color depends on the amount) indicates the extra-framework octahedral form. But for a specific estimation, we use the ratio of intra-framework Fe to extra-framework Fe or $A_{\text{UV}}/A_{\text{VIS}}$ ratio to judge which synthesis condition yields the best Fe-MPS powder as a UV protecting agent. As shown in **Table 2**, a powder with a higher A_{UV} and a higher $A_{\text{UV}}/A_{\text{VIS}}$ ratio is considered the better UV protecting agent. First, we performed a demonstration test to confirm the photo-

Fig. 2 Ultraviolet-visible absorbance spectra of Fe in the tetrahedral form (FeO_4^- , sample no.1, line 1) and Fe in the octahedral form (Fe_2O_3 , admixture of Fe_2O_3 and mesoporous silica, line 2).

properties of Fe and the results are shown in **Fig. 2**. Generally, coordination of iron (III) oxide (Fe_2O_3 , Fig. 2 line 2) is in the octahedral form and it absorbs visible region light showing dark red to brown color. Contrastingly, it is known that when Fe is incorporated into silica framework of MPS, the coordination of Fe takes the tetrahedral form (FeO_4^-), and its photo-absorption property shifts from the visible region to the ultraviolet region (Fig. 2 line 1).

3.2.1 Effects of Fe sources

First, we examined the effects of the type of Fe source used in the synthesis; the results are shown in **Fig. 3**. For all samples using $\text{Fe}(\text{acac})_3$ as the Fe source it was mixed with TEOS in alcoholic phase, while in case of $\text{Fe}(\text{NO}_3)_3$ it was dissolved in water phase as stated in the experimental section. Results from Fig. 3 showed that when Fe is tetrahedrally incorporated into the silica network, it absorbs ultraviolet radiation with maximum absorption peaks at 220 and 260 nm comparing to Fe free MCM-41 type MPS (Fig. 3 line 3). Contrastingly, extra-framework octahedral Fe oxide which was synthesized by simple ion exchange of Fe ion into Al-MCM-

Fig. 3 Ultraviolet-visible absorbance spectra of Fe-MCM-41 (Fe/Si = 0.02) synthesized by $\text{Fe}(\text{acac})_3$ (sample no.1, line 1) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (sample no.2, line 2). And those spectra of Fe free MCM-41 (line 3) and Fe/Al-MCM-41 (line 4).

41 and subsequent calcination was brown, and the visible absorption was high (Fig. 3 line 4). Moreover, sample no.2 (Fig. 3 line 2), which was synthesized using $\text{Fe}(\text{NO}_3)_3$, showed ultraviolet absorbance equal to that of sample no.1 (Fig. 3 line 1), which was synthesized using $\text{Fe}(\text{acac})_3$. However, sample no.2 showed relatively high absorbance in the visible region and was light brown in color, which indicated that extra-framework octahedral Fe oxide were formed ($A_{\text{UV}}/A_{\text{VIS}}$ ratio were 3.45 and 1.91 for sample no.1 and 2 subsequently). It is possible that $\text{Fe}(\text{NO}_3)_3$ was hydrolyzed so rapidly that large amounts of ferric hydroxides ($\text{Fe}(\text{OH})_3$) were produced and transformed into the extra-framework octahedral iron oxides, which are more stable than the intra-framework tetrahedral form, resulting in higher visible absorbance. On the other hand, $\text{Fe}(\text{acac})_3$ was slowly hydrolyzed, thereby generating ferric hydroxides at a slow rate and resulting in lower amounts of the extra-framework octahedral form and lower visible absorbance.

3.2.2 Effects of template removal method

Next, we examined effects of the various template removal methods. Calcination in dry air is known as a conventional method to remove the organic template from a mesoporous silica structure, but it has been reported that the mesoporous structure could collapse at high temperatures^{26,27}. Because the extra-framework Fe oxide is usually formed at a high temperature, we had considered this method to be possibly unfavorable. For comparison, we used the solvent extraction method that is less destructive and is recyclable^{28,29}. Refluxing with ethanol is generally used for MPSs that do not contain metals; but in some cases, especially for Fe-MCM-41, HCl is required to completely extract the templates that are bound to the metal ions²⁹. From **Fig. 4**, we concluded that the calcination method (sample no.1, Fig. 4 line 1) yielded the powder with higher ultraviolet absorption, but visible absorption was detected.

Fig. 4 Ultraviolet-visible absorbance spectra of Fe-MCM-41 (Fe/Si = 0.02) synthesized by $\text{Fe}(\text{acac})_3$ of which the surfactants were removed by calcination method (sample no.1, line 1), solvent extraction method (sample no.3, line 3), mixed method (sample no.4, line 4) comparing to the as-synthesized one (line 2).

Fig. 5 Ultraviolet-visible absorbance spectra of Fe-HMS (Fe/Si = 0.02) synthesized by $\text{Fe}(\text{acac})_3$ of which the surfactants were removed by calcination method (line 1, sample no.9), solvent extraction method (line 2, sample no.11) comparing to Fe free HMS (line 3).

However, data in Table 1 suggests that the mesoporous structure did not collapse. It can be concluded that calcination at a high temperature caused the intra-framework tetrahedral Fe coordination to change to the extra-framework octahedral Fe oxides, resulting in increased visible absorbance. As compared to the calcined sample, the solvent-extracted sample (sample no.3, Fig. 4 line 3) showed no visible absorption but lower ultraviolet absorption. This indicates that solvent extraction, which was performed at a low temperature, did not cause the intra-framework tetrahedral Fe coordination to change to the extra-framework octahedral Fe oxides ($A_{\text{UV}}/A_{\text{VIS}}$ ratio were 3.45 and 2.77 for sample no.1 and 3 respectively). Nevertheless, because HCl was used in extraction, tetrahedral Fe was also

Fig. 6 Ultraviolet-visible absorbance spectra of calcined Fe-MCM-41 synthesized by $\text{Fe}(\text{acac})_3$ of which Fe/Si mole ratio in mixtures were 0.01 (sample no.5, line 1), 0.02 (sample no.1, line 2) and 0.05 (sample no.7, line 3).

extracted, resulting in the decrease in ultraviolet absorption. Comparing to MCM-41, HMS which is synthesized by using dodecylamine as the template could be extracted easily by ethanol without HCl resulting in no decrease in ultraviolet absorbability (sample no.11, **Fig. 5** line 2).

3.2.3 Effects of Si/Fe molar ratios

Next, we examined the effects of the Fe amount by increasing the Fe/Si molar ratios (in the mixture) from 0.01 to 0.02 and 0.05 (sample nos.5, 1, and 7 respectively). The results are shown in **Fig. 6**. When the Fe/Si molar ratio (in the mixture) was increased, ultraviolet absorbance increased ($A_{\text{UV}}/A_{\text{VIS}}$ ratio were 4.79, 3.45 and 2.58 for sample nos.5, 1 and 7 respectively). However, the ultraviolet absorbance of sample no.7 did not increase as expected and the visible absorbance increased. According to these results, it can be said that the amount of intra-framework Fe was limited. Moreover, some of the excess Fe ions were washed away and some were transformed into extra-framework octahedral Fe oxides, resulting in increased visible absorption. We can also confirm from the results shown in Table 1 that the surface area of sample no.7 decreased, which is considered to be a result of extra-framework octahedral Fe oxide inside the mesopores.

3.2.4 Effects of type of mesoporous silicas

Fig. 7 shows absorbance spectra of various types of Fe-containing mesoporous silicas. The visible absorbance of Fe-MCM41 (sample no.1) and Fe-HMS (sample no.9) was low, but the ultraviolet absorbance of sample no.1 was higher than that of sample no.9. For Fe-SBA15 (sample no.17), the visible absorption peak was high while the ultraviolet absorption peak was relatively low as compared to that of sample no.1 ($A_{\text{UV}}/A_{\text{VIS}}$ ratio were 3.45, 2.57 and 1.35 for sample nos.1, 9 and 17 respectively). These results could be explained by the fact that negative charges of the intra-framework tetrahedral

Fig. 7 Ultraviolet-visible absorbance spectra of different types of Fe containing mesoporous silicas, Fe-MCM-41 (sample no.1, line 1), Fe-HMS (sample no.9, line 2) and Fe-SBA-15 (sample no.17, line 3); all were calcined samples with Fe/Si mole ratio = 0.02.

Fig. 8 Ultraviolet-visible absorbance spectra of Fe-MCM-41 (sample no.1, line 1) comparing to Fe-silica (sample no.21, line 2); all were calcined samples with Fe/Si mole ratio = 0.02.

Fe (FeO_4^-) were stabilized by positive charges of the surfactants used in the synthesis of sample no.1. Furthermore, the basic environment used in the synthesis of sample no.1 (pH of 11) caused the generation of silica ions (isoelectric point of Si = 2) to occur rapidly, which led to prompt introduction of Fe into the silica framework. On the other hand, the surfactants used in the syntheses of sample nos.9 and 17 were non-polar, which led to no stabilization effects. Moreover, sample nos.9 and 17 were synthesized in neutral and acid conditions, respectively, in which the silica network was formed slowly; therefore, Fe compounds were hydrolyzed and turned into extra-framework octahedral Fe oxides before the silica network was synthesized, causing low ultraviolet absorbance and high visible absorbance.

In order to determine how important the stabilization effect of the cation surfactant is, Fe-MCM-41 (sample no.1) and Fe-containing nonporous silica (sample no.21) were synthesized and compared based on their ultraviolet visible spectra (see Fig. 8). As a result, sample no.21 demonstrated lower ultraviolet absorbance than sample no.1 while there was no difference in visible absorbance. These results can be explained by the similar explanation given above – the cation surfactants used to form the mesoporous structure helped incorporate Fe into the silica network by charge stabilization.

3.3 Potential as a UV protecting agent

Based on all the results, it can be proposed that a favorable method for synthesizing an iron-containing mesoporous silica with high ultraviolet absorption would be to use $\text{Fe}(\text{acac})_3$ to synthesize Fe-MCM-41 and subsequently remove the template by calcination (sample no.1). However, we need to consider not only the UV absorbability of the synthesized powder based on ultraviolet-visible diffuse reflectance spectra but we should consider that thin films of UV protecting samples should not let UV pass through as well. In order to obtain those uniform thin films, aqueous slurries of the samples were prepared and applied at thicknesses of 23.6 μm on glass slides as the best method for yielding uniform and repeatable thin films. Then, the UV transmittance (290–400 nm) of those thin films was measured. Finally, as general UV absorbing agents tend to be photo-catalysts, thus photo-catalytic activities should be measured as well in order to confirm that these suggested UV absorbers do not exhibit photo-catalytic activity.

3.3.1 UV transmittance of thin films of water slurries of samples

The Fe-MPS samples in each aqueous slurry preparation were dispersed with maximum contents in order to estimate their maximum ultraviolet protection capabilities. As shown in Figs. 9 and 10, ultraviolet radiation transmittance (290–400 nm) of the thin films of 25%w aqueous slurries of Fe-MPSs (sample nos.5, 1, and 7) were measured in comparison to those of 25%w aqueous slurries of Fe-free MCM-41 (Fig. 9 line 3, 2, 4 and 1 respectively) and those of 60%w aqueous slurries of silica surface treated TiO_2 (Fig. 10 line 2). UV transmittance became lower when Fe/Si ratio increased. Nevertheless, those of sample no.7 (Fe/Si molar ratio = 0.05) did not decrease linearly from sample no.1 (Fe/Si molar ratio = 0.02). As explained above in section 3.2.3 (Fig. 6), the introducible capacity of Fe in MCM-41 is limited. Moreover, Fe-MPS aqueous slurry films showed low UV transmittance in both UVA (320–400 nm) and UVB (290–320 nm). In general, UVA transmittances were slightly higher comparing to that of silica surface treated TiO_2 . However, the result showed that the UV transmittance of 23.6 μm films of 25%w aqueous slurries of the suggested calcined Fe-MPS (Fe/Si mole ratio = 0.02) were equal to that of 60%w silica surface treated TiO_2 aqueous

Fig. 9 Ultraviolet transmittance spectra (290–800 nm) of Fe-MCM-41 (line 2, 3, 4 for sample nos.5, 1 and 7) comparing to Fe-Free MCM-41 (line 1).

Fig. 10 Ultraviolet transmittance spectra (290–800 nm) of silica treated TiO_2 (line 2) comparing to Fe-Free MCM-41 (line 1).

slurry. Comparing the results of UV transmittances, visible transmittance (400–800 nm) of Fe-MCM-41 aqueous slurry film is higher than that of silica surface treated TiO_2 aqueous slurry film.

These results can be explained by considering that TiO_2 reflects the entire range of visible light, therefore its transmittance curve is horizontal along 400–800 nm and its color is pure white (Fig. 10 line 2). On the other hand, Fe-MCM-41 is transparent and slightly yellow in color, therefore the transmittance is high at long wavelength area and low at short wavelength area (Fig. 9 line 2–4). Fe free MCM-41 aqueous slurry film (Figs. 9, 10 line 1) is transparent and it was found that it did not absorb or reflect either visible light or UV ray so the transmittance of its film was totally horizontal at about 100%.

Besides, as shown in Table 4, we confirmed the UV protecting ability of Fe-MPS by calculating SPF and PA values from the UV transmittance data. Fe-MCM-41 absorbed not only UVB (320–400 nm) but also UVA (290–320 nm). The SPF values of sample nos.5, 1, and 7 were 7, 22, and 37, respectively, while the PA values were PA+, PA++, and PA+++, respectively. In comparison, the SPF and PA values

Table 3 Photocatalytic activity measured by the photodegradation of D&C red no.6 solutions.

Samples ^a	Absorvances of D&C red no.6 solutions		%Fade ^c
	UV irradiated ^b	Dark	
TiO ₂ (anatase form)	0.45	2.36	80.93
Silica surface treated TiO ₂	2.55	2.66	4.14
no.5	1.98	1.98	0.00
no.1	2.29	2.29	0.00
no.7	2.31	2.31	0.00
no.11	1.84	1.84	0.00
no.12	1.95	1.96	0.51
no.9	1.84	1.85	0.54
no.14	1.89	1.89	0.00
no.19	0.41	0.42	2.38
no.17	0.47	0.49	4.08
no.20	0.83	0.90	7.78

^a Synthesis conditions of each sample can be referred from Table 1.^b Irradiation was performed by 10W black light lamp (80 μ W/cm²).^c %Fade

$$= \frac{(\text{absorbance of UV irradiated sample} - \text{absorbance of dark kept sample}) \times 100}{\text{absorbance of dark kept sample}}$$

of silica surface treated TiO₂ were SPF22 and PA++. For Fe-HMS, SPF values of sample nos.11, 12, 9, and 14 were 18, 4, 17, and 22, respectively, while the PA values were PA++, PA, PA+, and PA+++, respectively. However, for Fe-SBA-15 (sample nos.19, 17, and 20), the SPF and PA values were no more than 7 and PA++; the possibility of Fe-SBA-15 as a sunscreen agent was less than that of Fe-MCM-41 and Fe-HMS.

From these results, we can conclude that there is enough potential for Fe-MPS as a UV protecting agent but in order to evaluate it as a sunscreen agent, SPF and PA values test should be performed in vivo by applying sunscreen to the skin of a volunteer and measuring how long it takes before sunburn occurs when exposed to an artificial sunlight source and comparing to the reference (without sunscreen)^{31,33,34}. However, in this study we only need to preliminarily screen the UV protection capabilities of Fe-MPSs, thus we performed in vitro tests by measuring the actual UV transmittances of 25% aqueous slurry films of samples and calculating the values by the equation stated in the characterization part.

3.3.2 Photocatalytic activity

In general, ultraviolet absorption activity is related to photo-catalytic activity and, particularly in the cosmetic field, photo-catalytic activity is known as one of the causes of oil and pigment degradation, which causes unfavorable appearance and shortened product shelf life³⁰. Therefore, photo-catalytic activity tests are necessary to determine certain qualities of a cosmetic sunscreen material. **Table 3** shows the measured photo-catalytic activity of titanium dioxide (anatase form) tested by D&C red No.6 solution fading. The maximum absorbance of the ultraviolet irradiated sample was 0.45, which was a 80.93% decrease from that of the reference,

Table 4 SPF and PA values of water slurry prepared samples.

Samples ^a	Max. despersible amount ^d (%w/w)	SPF ^b	PA ^c	color appearance
Silica surface treated TiO ₂	60%	22	PA++	white
Fe free MCM-41	25%	1	PA	white
no.5	25%	7	PA+	white
no.1	25%	22	PA++	pale yellow
no.7	25%	37	PA+++	slightly brown
Fe free HMS	25%	1	PA	white
no.11	25%	18	PA++	white
no.12	25%	4	PA	white
no.9	25%	17	PA+	white
no.14	25%	22	PA+++	white
Fe free SBA-15	25%	1	PA	white
no.19	25%	2	PA	pale yellow
no.17	25%	4	PA+	pale yellow
no.20	25%	7	PA++	slightly brown

^a Synthesis conditions of each sample can be referred from Table 1.^{b,c} SPF and PA stand for Sun Protection Factor and protection grade of UVA respectively.^d The maximum amounts of sample that can be dispersed in water.

2.36. For comparison, the photo-catalytic activity of a silica surface treated titanium dioxide, which is presently used as a sunscreen agent, was tested under the same conditions and was found to fade at 4.14%. However, the photo-catalytic activity measurement of sample no.1, which yielded the best photo-absorption profile, showed no difference in the maximum absorbance between the ultraviolet-irradiated sample and the reference. There was also no significant photo-catalytic activity detected for the Fe-HMS samples, although a less than 1% fading was found in both sample no.9 and 12. However, compared to Fe-MCM-41 and Fe-HMS, Fe-SBA-15 showed a small, but detectable, amount of photo-catalytic activity, especially in sample no.20, which showed 7.78% fading.

4. Conclusions

One-step synthesized Fe-containing mesoporous silicas (Fe-MPSs) show differences in ultraviolet absorption capabilities and color depending on their synthesis conditions. Among MCM-41, HMS and SBA-15 type Fe-MPSs, it can be said that in order to synthesize Fe-MPS with high UV absorption capability, MCM-41 type Fe-MPS using Fe(acac)₃ as the iron source and removing the template by calcination is preferred. Even though its color is slightly brown, this method is recommended for general applications because of its high ultraviolet absorption capability. However, solvent extracted MCM-41 and HMS type Fe-MPS synthesized via Fe(acac)₃ is suggested in case of applications for colorless preparations even though its ultraviolet absorption capability is lower than MCM-41 type. Moreover, the UV transmittances of the thin films of 25%w aqueous slurries of the suggested calcined Fe-MPS (Fe/Si mole ratio = 0.02) were equal to the one of

60%w silica surface treated TiO₂ aqueous slurry. Incidentally, samples synthesized by both proposed methods did not demonstrate photo-catalytic activity (measured via photo-degradation of D&C red no.6 solution), Therefore, Fe containing mesoporous silicas synthesized by both proposed methods have the potential for uses as new UV protecting agents.

5. Acknowledgements

This research was partially supported by the Ministry of Education, Science, Sports and Culture of Japan under a Grant-in-Aid for Scientific Research (C), 22550173, 2010.

References

- 1) L. L. Hruza, A. P. Pentland: *J. Invest. Dermatol.*, **100** (Suppl.), 35S (1993).
- 2) B. A. Gilchrist, H. Y. Park, M. S. Eller, M. Yaar: *Photochem. Photobiol.*, **63**, 1 (1996).
- 3) K. C. Farmer, M. F. Naylor: *Ann. Pharmacother.*, **30**, 662 (1996).
- 4) B. A. Gilchrist: *Br. J. Dermatol.*, **135**, 867 (1996).
- 5) A. O. Gamer, E. Leibold, B. van Ravenzwaay: *Toxico. in Vitro*, **20**, 301 (2006).
- 6) G. P. Dransfield: *Radiat. Prot. Dosimetry*, **91**, 271 (2000).
- 7) V. Davide, P. Tatiana, M. E. Carlotti: *J. Cosmet. Sci.*, **54**, 513 (2003).
- 8) M. D. Newman, M. Stotland, J. I. Ellis: *J. Am. Acad. Dermatol.*, **61**, 685 (2009).
- 9) S. R. Pinnell, D. Fairhurst, R. Gillies, M. A. Mitchnick, N. Kollias: *Dermatol. Surg.*, **26**, 309 (2000).
- 10) P. J. Barker, A. Branch: *Progr. Org. Coatings*, **62**, 313 (2008).
- 11) A. Tuel, I. Arconb, J. M. M. Milleta: *J. Chem. Soc., Fara. Trans.*, **94**, 3501 (1998).
- 12) Y. Li, Z. Feng, Y. Lian, K. Sun, L. Zhang, G. Jia, Q. Yang, C. Li: *Micropor. Mesopor. Mater.*, **84**, 41 (2005).
- 13) M. Stockenhuber, M. J. Hudson, R. W. Joyner: *J. Phys. Chem. B.*, **104**, 3370 (2000).
- 14) S. K. Badamali, P. Selvam: *Catalysis Today*, **141**, 103 (2009).
- 15) A. B. Bourlino, M. A. Karakassides, D. Petridis: *J. Phys. Chem. B.*, **104**, 4375 (2000).
- 16) P. Decyk: *Catalysis Today*, **114**, 142 (2006).
- 17) X. S. Zhao, G. Q. Lu, Graeme J. Millar: *Ind. Eng. Chem. Res.*, **35**, 2075 (1996).
- 18) M. H. Nilsen, E. Antonakou, A. Bouzga, A. Lappas, K. Mathisen, M. Stocker: *Micropor. Mesopor. Mater.*, **105**, 189 (2007).
- 19) P. Decyk, M. Trejda, M. Ziolk: *C. R. Chimie*, **8**, 635 (2005).
- 20) C. Amata, T. Yuka, S. Masashi: *Chem. Lett.*, **40**, 693 (2011).
- 21) R. Schmidt, D. Akporiaye, M. Stocker, O. H. Ellestad: *J. Chem. Soc., Chem. Commun.*, 1493 (1995).
- 22) P. T. Tanev, M. Chibwe, T. J. Pinnavaia: *Nature*, **368**, 321 (1994).
- 23) T. Takenouchi, Y. Kawano, Y. Takauchi, Y. Kohno, K. Takagi, M. Shibata: *J. Jpn. Soc. Colour Mater.*, **84**, 308 (2011).
- 24) C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck: *Nature*, **359**, 710 (1992).
- 25) A. Katiyar, S. Yadav, P. G. Smirniotis, N. G. Pinto: *J. Chromatogr. A*, **1122**, 13 (2006).
- 26) F. Kleitz, W. Schmidt, F. Schüth: *Micropor. Mesopor. Mater.*, **44**, 95 (2001).
- 27) F. Kleitz, W. Schmidt, F. Schüth: *Micropor. Mesopor. Mater.*, **65**, 1 (2003).
- 28) H. Ji, Y. Fan, W. Jin, C. Chen, N. Xu: *J. Non-Cryst. Solids*, **354**, 2010 (2008).
- 29) Y. K. Bae, O. H. Han: *Micropor. Mesopor. Mater.*, **106**, 304 (2007).
- 30) V. Brezová, S. Gabčová, D. Dvoranová, A. Staško: *J. Photochem. Photobiol. B Biol.*, **79**, 121 (2005).
- 31) D. R. Sambandan, D. Ratner: *J. Am. Acad. Dermatol.*, **64**, 748 (2011).
- 32) Z. Gabelica, S. Valange, M. Shibata, H. Hotta, T. Suzuki: *Micropor. Mesopor. Mater.*, **44-45**, 645 (2001).
- 33) <http://www.aad.org/media-resources/stats-and-facts/prevention-and-care/sunscreens> (last accessed on June 4, 2012)
- 34) <http://www.fda.gov/Drugs/ResourcesForYou/Consumers/BuyingUsingMedicineSafely/UnderstandingOver-the-CounterMedicines/ucm258468.htm> (last accessed on June 4, 2012)
- 35) A. L. Roe, D. J. Schneider, R. J. Mayer, J. W. Pyrz, J. Widow, L. Que Jr.: *J. Am. Chem. Soc.*, **106**, 1676 (1984).
- 36) R. S. Weber: *J. Catal.*, **151**, 470 (1995).

種々の方法で合成した鉄含有メソポーラスシリカの紫外線吸収能

アマタ・チャイケンカイ*・竹下侑花*・柴田雅史*†

*東京工科大学応用生物学部 東京都八王子市片倉町1404-1 (〒192-0982)

† Corresponding Author, E-mail: mshibata@bs.teu.ac.jp

(2012年4月9日受付；2012年9月24日受理)

要 旨

Fe源、構造形成剤の除去方法およびメソポーラスシリカの型がFe含有メソポーラスシリカの紫外線吸収能に与える影響を検討した。また、これらFe含有メソポーラスシリカの紫外線防御剤としての可能性を、薄膜にしたときの紫外線透過性、外観色、光触媒活性により評価した。

FeアセチルアセトナートをFe源としたMCM-41型を焼成した試料が最も良好な紫外線吸収能を示した。ただし、鉄濃度が高くなる(Fe/Si ≥ 0.02)と薄茶色の外観となった。一方、FeアセチルアセトナートをFe源としたHMS型またはMCM-41型で溶媒抽出によって構造形成剤を除去した試料は紫外線吸収能は前述のものより劣るものの外観色は白色であった。

焼成したFe-MPS試料(Fe/Siモル比=0.02)の水分散物の薄膜は、シリカ表面処理をした酸化チタン水分散物と同程度の紫外線透過挙動であった。また光触媒活性もみられなかった。これらのことからFe含有メソポーラスシリカは紫外線吸収剤としての可能性があるものと考えられる。

キーワード：Fe含有メソポーラスシリカ、紫外線防御剤、紫外線吸収能、光触媒活性