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Synthesis of Iron-containing Mesoporous Silica Aiming to Use as a New Sunscreen Ultraviolet Absorber

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The relationship between synthesis conditions of iron-containing mesoporous silica (Fe-MCM-41) and UV–visible absorbance was studied. Fe-MCM-41 with high UV absorption and low visible absorption was effectively synthesized by using [Fe(acac)$_3$] as an iron source and employing calcination for the template removal. The obtained Fe-MCM-41 did not exhibit photocatalytic activity as determined by dye decomposition, and its SPF and PA values were at an acceptable level, concluding that there is a possibility as a new sunscreen agent.

To block solar ultraviolet radiation consisting of UVA (400–315 nm) and UVB (315–280 nm) which cause damage to skin,[1–4] sunscreens are applied. Recently, there have been attempts to develop new inorganic sunscreen agents which overcome the defects of currently used TiO_2 and ZnO powders such as visible light reflectance and photocatalytic activity.[5–7] The desirable properties of these new agents are high absorbance of both UVA and UVB but low absorbance and reflectance of visible light. Furthermore, photocatalytic activity should be absent.

Many types of mesoporous silica (MPS), a silica framework with nanosized pores, are presently researched in various fields such as catalytic chemicals and adsorptive separation[8] because of their high surface area and well-ordered controllable pores.[9] In addition to those well-known uses, MPS has two promising properties for sophisticated cosmetic ingredients. The first is that MPS powder readily suspends in both water and organic mediums and can be used as auxiliary emulsifier for cosmetics. The second is that it can contain heterometal ions in its framework or on exchangeable cation sites by which we can modify the physicochemical properties of those heterometal species. Some metals are useful for cosmetics such as Al,[10] Fe,[11,12] Ti,[13] and Zn.[11]

Among metal-containing MPS, iron-containing (Fe-MPS), of which acidic or partial oxidation catalytic activities have been examined by many researchers,[14] shows the appearance of color variation depending on the state of Fe. When Fe exists outside the framework, the appearance is brown, but when it is inserted into the framework it becomes white. This phenomenon is related to the absorbance band shifting from the visible to UV region. Although as catalyst, this color variation is only useful as a simple confirmation whether Fe-MPS was successfully synthesized or not, we are especially interested in its use as a new ultraviolet absorbing agent. In other words, by the combination of the optical properties of Fe in the framework and the physical properties of MPS itself, Fe-MPS can overcome the deficits of existing inorganic sunscreen agents mentioned above.

In this paper, we studied the relationship between synthesis conditions and UV–vis absorbance of Fe-MPS. In particular, the iron-containing mobil crystalline materials-41 (Fe-MCM-41) was selected. Species of Fe source and template removal procedure were varied. We also examined the photocatalytic activity of Fe-MCM-41 which is the deficit of most concern of inorganic materials as cosmetic ingredients. Finally, sun protection factor (SPF) and protection grade UVA (PA) values[15] of Fe-MCM-41 were evaluated, and we explored the possibility of Fe-MCM-41 as a new inorganic sunscreen agent.

All materials in this study, except those specified, were of analytical grade from Wako Chemical and used as received. Hexadecyltrimethylammonium bromide (C16TMABr, 2.28 g) was dissolved in 44.3 g of purified water and stirred at 313 K for 1 h (solution A). 10.29 g of tetraethyl orthosilicate (TEOS) was mixed with tris(acetylacetonato)iron(III) ([Fe(acac)$_3$], Kanto Chemical Co., Fe/Si molar ratio = 0.01, 0.02, or 0.05), and sufficient amount of ethanol was added (solution B). When iron(III) nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) was used as Fe source, it was dissolved in solution A. 0.58 g of NaOH in 6.3 g of purified water and solution B were alternatively added dropwise into solution A within 15 min while the mixture was vigorously stirred at room temperature. After stirring for an additional 2 h, the temperature was increased to 413 K and kept static for 48 h. The obtained Fe-MCM-41 was recovered, washed until the pH becomes 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. The first was the calcination at 873 K for 6 h under air blasting. The second was solvent extraction of which 4 g of as-synthesized product was stirred for 6 h in a solution prepared by mixing 300 mL of ethanol with 2 mL of 2 M HCl. This process was repeated twice. The third was a mixture of these two procedures: solvent-extracted Fe-MCM-41 was calcined for 6 h at 873 K.

Nitrogen sorption measurement was performed on a Shimadzu Tristar 3000. Surface area was calculated by the Brunauer–Emmett–Teller (BET) method. Pore size and pore volume were determined by Barrett–Joyner–Halenda (BJH) method using the peak of desorption branch. Scanning electron microscopic images were taken with a JEOL JSM-6060LV. UV–visible diffuse reflectance spectra were observed on a JASCO V-650 spectrophotometer equipped with an integrating sphere ISV-722.

Photocatalytic activity of Fe-MCM-41 was estimated by the color fade of azo dye solution (F&D red No. 6, Daito Kasei Kogyo Co.). 0.01 g of anatase TiO_2 powder (as a standard of photocatalyst) or 0.025 g of Fe-MCM-41 was dispersed in 3.0 g of dye solution (max absorbance at 493 nm was around 3) and transfered to a glass petri dish (ϕ 3 cm). The mixture was exposed to a UV lamp (10 W Toshiba black light; 80 $\mu W\,cm^{-2}$) with stirring while the reference was stirred in the dark. After 30 min, they were recovered and the absorbance values of the supernatant were measured. The photocatalytic activity was estimated by the absorbance change at 493 nm through UV irradiation.

Table 1. Appearance and surface properties of iron-containing mesoporous silica (Fe-MPS) via [Fe(acac)$_3$]

Sample	Color	S_{BET}[b] /$m^2\,g^{-1}$	Pore d[c] /nm	Pore V[d] /$cm^3\,g^{-1}$
Fe-MCM-41(C)-0.01	white	1038	3.20	1.00
Fe-MCM-41(S)-0.01	white	1045	3.07	0.99
Fe-MCM-41(C)-0.02	off-white	960	2.83	0.87
Fe-MCM-41(S)-0.02	white	943	3.03	0.90
Fe-MCM-41(C)-0.05	pale yellow	385	2.67	0.27
Fe-MCM-41(S)-0.05	pale yellow	561	2.75	0.43

[a]Sample names are referred to calcined (C), solvent extraction (S), and numbers shown are Fe/Si mole ratio. [b]Surface area calculated by the Brunauer–Emmett–Teller (BET). [c]Pore diameter and [d]pore volume determined by Barrett–Joyner–Halenda (BJH) method using the peak of desorption branch of the isotherm.

To measure SPF and PA, Fe-MCM-41 was dispersed in purified water (60%w/w) with a mixer (Vortex Genie 2). Then, it was applied to a quartz glass plate at a thickness of 23.6 µm and then dried in air. The UV transmittance of the obtained powder film was measured on a JASCO V-650, and the SPF and PA values were simply estimated by using SPA•PA value calculation program JASCO VWSP-787.

As a result, surface and mesopore properties of Fe-MPSs are shown in Table 1. All samples had high surface area ($>800\,cm^2\,g^{-1}$) considering that they can be dispersed well in cosmetic mediums except for Fe-MCM-41-0.05 of which surface area was 385 or 561 $m^2\,g^{-1}$ for calcined and solvent-extracted product, respectively, which can result from iron oxide aggregated at extraframework. All samples were aggregated spheres of which initial particle size was around 0.5 µm observed by SEM. However, when iron content was increased to Fe/Si = 0.05, they became rather smaller (0.3 µm).

As is known, when Fe is introduced into silica frameworks, the spectroscopic properties will change. Intraframework tetrahedral iron (FeO_4^-) absorbs UV around 220 and 260 nm resulting from electronic transition[16] from ligands to the t_{2g} and e_g orbitals of Fe^{3+}. A broad peak around 300 nm corresponds to octahedral iron oxide that locates at extraframework of MPS,[17] while a broad visible absorption band above 400 nm is caused by iron oxide clustering outside the framework.[16] A desirable photochemical property of Fe-MCM-41 as a sunscreen agent is to possess a high absorption band in the UV area (220–260 nm) without absorbance in the visible region (above 400 nm).

Figure 1a shows the UV–visible spectra of calcined Fe-MCM-41 (Fe/Si = 0.02) of which the iron source was [Fe(acac)$_3$] or Fe(NO$_3$)$_3$. Peaks at 220 and 260 nm were distinct in both samples indicating tetrahedral intraframework Fe was obtained. When Fe(NO$_3$)$_3$ was used, the obtained powder was dark brown and the absorbance above 400 nm which corresponds to clustered iron oxide outside the framework was distinct while that synthesized from [Fe(acac)$_3$] was off-white, and the absorbance above 400 nm was far lower. This is presumably because the solubility of Fe(NO$_3$)$_3$ in water is higher than [Fe(acac)$_3$], so it can be easily converted to iron oxide which cannot be introduced into the framework. From this result, we concluded that [Fe(acac)$_3$] is suitable as a Fe source especially for the synthesis of Fe-MCM-41.

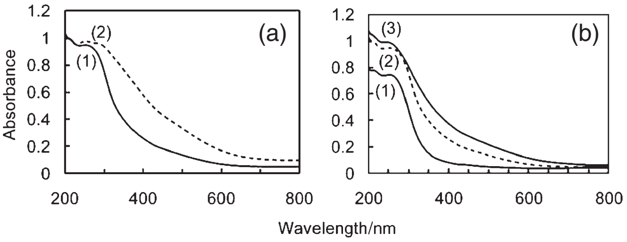

Figure 1. (a) UV–visible spectra of Fe-MCM-41 from different Fe sources (Fe/Si = 0.02, calcined): (1) via [Fe(acac)$_3$], (2) via Fe(NO$_3$)$_3$. (b) UV–visible spectra of Fe-MCM-41 varied on Fe/Si molar ratio = 0.01 (1), 0.02 (2), and 0.05 (3).

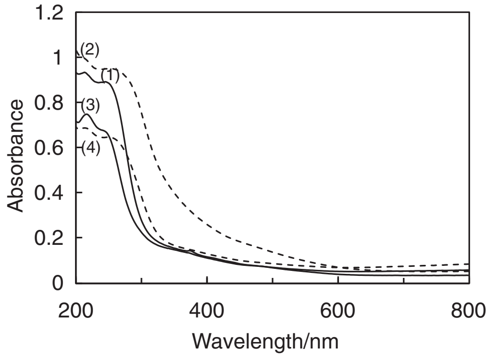

Figure 2. Variation of UV–vis spectra of Fe-MCM-41 (Fe/Si = 0.02) by surfactant removal method: (1) As-synthesized, (2) calcined, (3) solvent extracted, and (4) calcined after being solvent extracted.

The effect of Fe content is shown in Figure 1b. The UV absorbance of Fe-MCM-41 increased according to Fe/Si ratio. But the absorbance of Fe-MCM-41-0.05 was not as high ($Abs = 1.0$) as expected from extrapolation of the other two Fe-MCM-41s although Fe/Si ratio of those three samples simply estimated with EPMA equipped with SEM was almost the same as that of the ingredients. This indicates that there is a limit of introducible capacity of Fe into the framework. Actually, Fe-MCM-41-0.05 showed higher absorbance above 400 nm indicating that the excess of Fe caused clustered iron oxide outside the framework.

The removal of template by solvent extraction is known to be more eco-friendly and economical than calcination because the template can be recovered and recycled. UV–visible spectra of Fe-MCM-41-0.02 with various template removal methods are shown in Figure 2. Calcined sample showed rather higher absorbance above 400 nm than the as-synthesized material (without calcination), indicating that some parts of intraframework Fe changed into clustered iron oxide through calcination. On the other hand, that absorbance did not increase when solvent extraction was performed. However, the peak intensity at 220 and 260 nm decreased. We assume that the template removal by solvent extraction can prevent converting of intraframework Fe into clustered iron oxide but can cause partial Fe leakage from the framework especially of that located on the surface. It can be concluded that the solvent extraction is less suitable for the preparation of Fe-MCM-41. From these results, it can be concluded that in order to obtain Fe-MPS with high UV

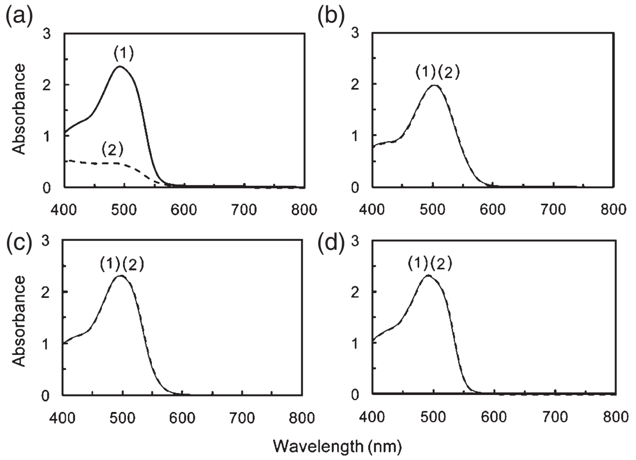

Figure 3. Fading of azo dye solution with (a) titanium dioxide (anatase form), (b) Fe-MCM-41-0.01, (c) Fe-MCM-41-0.02, and (d) Fe-MCM-41-0.05. Solid lines (1) are references (without irradiation) while dash lines (2) are after 30 min UVA exposure.

absorption and low visible absorption, Fe-MCM-41 prepared using [Fe(acac)$_3$] as an iron source and removing the template by calcination is the most suitable sample.

When the absorption of Fe-MPS shifts to shorter wavelength, photocatalyst activity tends to improve. Actually there have been some attempts to use Fe-MPS as a photocatalyst.[18]

However, for the use of sunscreen absorbing agents, photocatalytic activity is an undesirable property because it may decompose other organic ingredients in cosmetics such as dyes, oils, and surfactants. At first, photocatalytic activity of anatase TiO_2 which is known to be a strong photocatalyst was examined (Figure 3a). Maximum absorbance of azo dye at 493 nm was drastically decreased by 81% indicating that dye molecules in the dispersion were decomposed by the photocatalytic activity of TiO_2. Then the photocatalytic activity of Fe-MCM-41-0.01, -0.02, and -0.05 (calcined samples) were measured, the color of dye solutions was scarcely changed under the same irradiation conditions and the decrease of the maximum absorbance of azo dye was less than 2.3% (Figures 3b–3d). These results proved that photocatalytic activity of Fe-MCM-41 is sufficiently weak and that the effect against organic molecules coexisting in aqueous solution will not be an issue in practical applications.

Finally, we estimated SPF and PA values of Fe-MCM-41 samples which were prepared in the form of water slurries, the simplified formula of oil-free sunscreen products. Table 2 shows values of SPF and PA calculated based on the transmittance. SPF values of Fe-MCM-41-0.01, -0.02, and -0.05 were 5.5, 10.3, and 19.1, and PA values were PA+, PA++, and PA++, respectively. The values increased according to Fe/Si ratio, but those of Fe-MCM-41-0.05 were not as high as expected from extrapolation. It is compatible with the reflection spectra (Figure 1b), relating to the limitation of introducible capacity of Fe into the framework stated above. The SPF and PA values of Fe-MCM-41-0.05 are close to those of commercial ZnO powders indicating that Fe-MCM-41 has potential as a sunscreen agent.

Table 2. SPF and PA values based on UV transmittance spectra

Samples	SPF	PA
MCM-41(C)-Fe free	1.2	PA+
Fe-MCM-41(C)-0.01	5.5	PA+
Fe-MCM-41(C)-0.02	10.3	PA++
Fe-MCM-41(C)-0.05	19.1	PA++

In conclusion, one-step-synthesized Fe-MPS exhibited variations in UV–visible spectroscopy depending on synthesis conditions. In order to synthesize Fe-MPS with high UV absorption and low visible absorption, we reported that Fe-MCM-41 prepared using [Fe(acac)$_3$] as an iron source and removing the template by calcination was the most appropriate sample. Photocatalytic activity of Fe-MCM-41 in dye decomposition was not found, and SPF and PA values were acceptable. Accordingly, we conclude that there is a possibility of using Fe-MCM-41 as a new sunscreen agent.

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