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ScienceDirect

Catalysis Today 132 (2008) 146–152

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Surface hydrophilic–hydrophobic property on transparent mesoporous silica thin films containing chromium oxide single-site photocatalyst

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Abstract

Using a sol–gel/spin-coating method with organic template, the transparent mesoporous silica thin films containing chromium oxide moieties can be prepared on quartz plate. The spectroscopic characterization has revealed that these thin films contain isolated and tetrahedrally coordinated chromium oxide moieties (single-site photocatalyst) in their frameworks. Even before UV light irradiation these Cr-containing mesoporous silica (CrMS) thin films have demonstrated a hydrophilic surface property more strongly than Cr-containing non-porous silica films and mesoporous silica thin films without chromium oxide. Furthermore, the Cr-containing mesoporous silica thin films showed the super-hydrophilic property not only under UV light irradiation but also even under visible light irradiation from a fluorescent lamp. In the presence of ethylene gas, the polyethylene was successfully formed on the surface of the CrMS thin film under UV light irradiation. After the formation of polyethylene the surface property of the CrMS thin film was converted into hydrophobic while keeping its transparency. The isolated and tetrahedrally coordinated chromium oxide moieties are responsible for these photo-induced surface reactions.

Keywords: Mesoporous silica thin film; Chromium oxide; Single-site photocatalyst; Hydrophilic–hydrophobic property; Polyethylene synthesis

1. Introduction

Silica based porous materials such as zeolite and mesoporous silica have been studied to be utilized as the useful catalysts and catalyst supports. The transition metal oxide moieties incorporated within the porous silica materials can have unique coordination geometry and exhibit unique catalytic reactivity. For example, Ti-containing zeolite and mesoporous silica having an isolated tetrahedrally coordinated titanium oxide moieties can show the efficient and selective catalytic activities in the epoxidation of alkenes using H_2O_2 or O_2 as oxidizing agent [1,2]. Also Cr-containing zeolite and mesoporous silica having an isolated tetrahedrally coordinated chromium oxide moieties can promote the dehydrogenation of ethylbenzene to styrene using CO_2 [3,4]. These isolated metal oxide moieties (titanium oxide and chromium oxide moieties) included within silica matrix such as zeolite and mesoporous silica has unique local structure and photocatalytic property [5,6]. Recently, these isolated metal oxide moieties are named as single-site photocatalysts [6,7]. As the single-site photocatalyst, the Ti-containing zeolite and mesoporous silica can show the efficient and selective reactions under UV light irradiation for various reactions such as the reduction of CO_2 with H_2O [8–10], NO decomposition into N_2 and O_2 [11,12], and the selective photoepoxidation of alkene with O_2 [13]. On the other hands, Cr-containing mesoporous silica can show photocatalytic reactivity for highly selective oxidation of alkane not only under UV light irradiation but also visible light irradiation [14–16].

TiO_2 thin films have been utilized in many fields not only for their photocatalytic properties but also their super-hydrophilic properties [17], because these thin films often exhibit the unique surface properties different from TiO_2 powder. The zeolite and mesoporous silica including the single-site photocatalyst usually have the shape of fine power which is difficult to be managed.

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doi:10.1016/j.cattod.2007.12.041

Recently, the simpler method to synthesize mesoporous silica films has been developed using the spin-coating [18–20] and dip-coating [21] methods. By the addition of titanium ions within the mesoporous silica thin films it becomes possible to design of unique surface active sites in the modified spaces. In our previous study, it has been found that the design of Ti-containing mesoporous silica thin film embedded onto transparent materials would provide the attractive surface functionalized materials having such as surface hydrophilic properties [22]. However, these Ti-containing catalysts can operate as the photocatalysts only under UV light irradiation. Previously, we have found that Cr-containing mesoporous silica in the powder form can demonstrate the photocatalytic reactivity even under visible light irradiation [14–16]. It is vital to develop the photocatalysts which can operate efficiently under visible light irradiation. The photo-induced surface properties of Cr-containing mesoporous silica films under UV light and visible light irradiation are also of special interest.

In this paper, transparent Cr-containing mesoporous silica thin films have been prepared on quarts plate by the sol–gel/spin-coating method. Their local structures around the metal species as well as surface hydrophilic and hydrophobic properties have been investigated. Additionally, the design of the hydrophobic surface by using the polymerization of ethylene on Cr-containing mesoporous silica is also applied as a unique method for the modification of surface hydrophilic–hydrophobic property.

2. Experimental

2.1. Preparation of Cr-containing mesoporous silica thin films and polymerization

The Cr-containing mesoporous silica (CrMS) thin films deposited on the plate of quartz were prepared by the sol–gel/spin-coating method using tetraethyl orthosilicate (TEOS) and $Cr(NO_3)_6 \cdot 9H_2O$ as silica and chromium precursors, $C_{12}H_{25}(OCH_2CH_2)_4OH$ (Brij^{R}30) as surfactant, hydrochloric acid and ethanol (TEOS + $Cr(NO_3)_6$:Brij30:HCl:EtOH = 8:0.9:0.8:50) (TEOS:$Cr(NO_3)_6$ = 100:x; x = 0, 1, 2, 3, 5, 10). The mixtures were stirred for 10 min at 298 K, dripped onto a quartz substrate (10 mm × 10 mm × 1 mm), spread evenly and spun coated at a spinning rate of 4000 rpm in 500–700 nm [22]. Thus, obtained thin films were calcined in air at 723 K for 5 h to remove the surfactant from the film materials. The Cr-containing non-porous silica thin films were also prepared by the same method without using surfactant.

For the synthesis of polyethylene on the CrMS thin film, the CrMS thin film was placed in a quartz cell with a flat bottom connected to a vacuum line system, heated at 200 °C for 2 h under vacuum, exposed to O_2 atmosphere (60–100 Torr) at the same temperature for 2 h, and then finally degassed at 150 °C for 2 h. After evacuation, ethylene (2 Torr) was introduced into the cell at 0 °C and the system was irradiated with UV light using a 100 W high pressure mercury lamp for 24 h. The polyethylene with a thickness of around 250–300 nm was formed with this condition.

2.2. Characterization and measurement of contact angle of water droplet

The XRD patterns were recorded with a Rigaku Mini-flex using Cu Kα radiation of $\lambda = 1.5418$ Å. The XAFS spectra (XANES and EXAFS) were measured at the BL-7C facilities of the Photon Factory at the National Laboratory for High-Energy Physics, Tsukuba. A Si (1 1 1) double crystal was used to monochromatize the X-rays from the 2.5 GeV electron storage ring [23]. The Cr K-edge absorption spectra were recorded in the fluorescence mode at 295 K. In a typical experiment, the sample was loaded into the *in situ* cell having the plastic windows. The normalized spectra were obtained by a procedure described in previous literature [24] and Fourier transformation was performed on k^3-weighted EXAFS oscillations in the range of 3–10 Å^{-1}. FE-SEM micrograph was obtained with S-5200. The IR spectra were recorded with a Shimadzu FT-IR spectrometer at 295 K.

The water-repellency of the film surface was checked by the contact angle of pure water droplet (0.01 ml) using a contact angle meter DropMaster 300 of Kyowa Interface Science Co. Ltd. The film surface was irradiated with UV light using a 100 W high pressure mercury lamp (70 mW/cm^2) or visible light using a fluorescent lamp (interior lightning) (10 μW/cm^2) for 1 h or kept in the dark condition for 1 day before the measurement of the contact angle.

3. Results and discussion

3.1. Characterization

Fig. 1 shows the photo images of Cr-containing non-porous silica films fixed on quartz plate, Cr-containing mesoporous silica (CrMS) thin film fixed on quartz plate, and CrMS thin film (Cr/Si = 0.05) after polymerization. The synthesized CrMS thin film was well-fixed on the substrate of quartz plate and totally transparent like original quartz plate.

The X-ray diffraction patterns of the Cr-containing non-porous silica films and Cr-containing mesoporous silica (CrMS) thin films having various chromium contents are shown in Fig. 2. The CrMS thin films with Cr/Si ratio of 0.01–0.05, exhibit a diffraction peak at around 2–3 degree, indicating the presence of mesoporous structure, while the Cr-containing non-porous silica film exhibits no diffraction peak in this region. The d-spacing of CrMS thin film decreases with the chromium content in CrMS

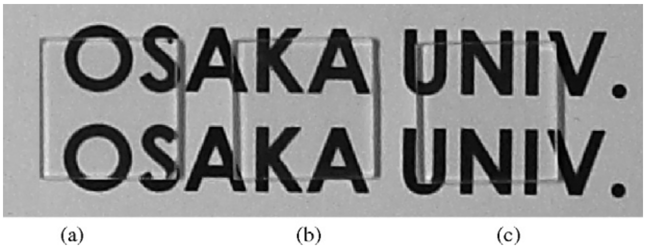

Fig. 1. Sample photography of quartz plates coated with (a) Cr-containing non-porous silica thin film; (b) Cr-containing mesoporous silica (CrMS) thin film; and (c) Cr-containing mesoporous silica (CrMS) thin film after polymerization.

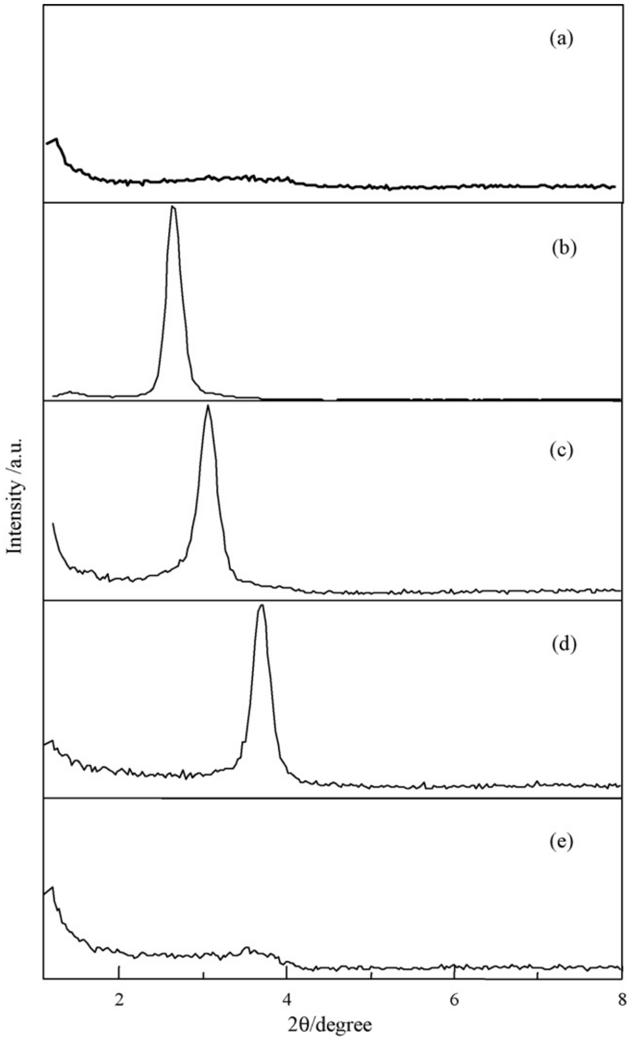

Fig. 2. XRD patterns of (a) Cr-containing non-porous silica thin film (Cr/Si = 0.01) and Cr-containing mesoporous silica (CrMS) thin films ((b) Cr/Si = 0.01; (c) 0.02; (d) 0.05; and (e) 0.1).

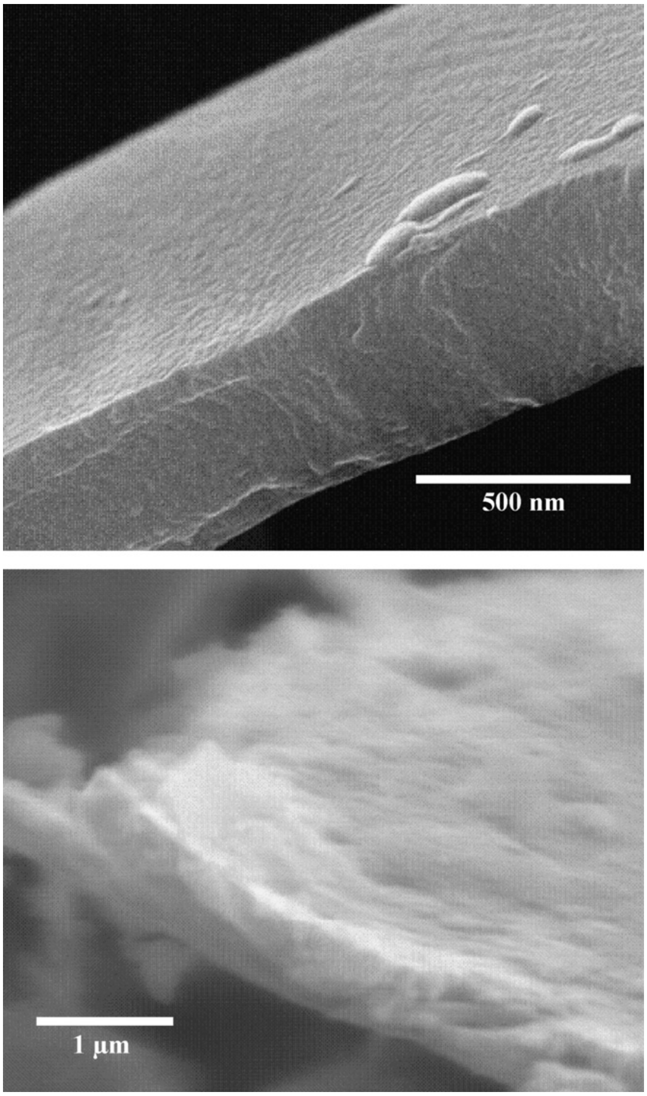

Fig. 3. FE-SEM images of Cr-containing mesoporous silica (CrMS) thin films (upper) before and (lower) after polymerization of ethylene.

thin films. On the other hand, the sample prepared with the Cr/Si ratio of 0.10 exhibits no peak due to the ordered mesoporous structure, indicating that mesoporous structure cannot be maintained after the calcination. The containing of the chromium oxide may induce the distortion of Si–O networks, because the chromium oxide moieties has Cr=O oxo bonding. The X-ray diffraction patterns of CrMS thin film exhibited no peak corresponding to crystalline phase at the higher angle, indicating that chromium oxide moieties are highly dispersed in the mesoporous structure, while no other crystalline phases are formed. These results indicate that the CrMS thin films with the Cr/Si ratio of 0.01–0.05 can be prepared having highly dispersed chromium oxide moieties on quartz plate by the present conventional sol–gel/spin-coating method.

Fig. 3 shows the field emission scanning electron microscopy (FE-SEM) image of the CrMS thin film before and after polymerization. Three-dimensional photo image of the sample did not show any cracks and abnormal large particles. The mean thickness of the CrMS thin film was determined to be ca. 500–700 nm.

Figs. 4 and 5 shows the XANES and FT-EXAFS spectra at the Cr K-edge of Cr-containing mesoporous silica (CrMS) thin films and reference compounds, respectively. The relative intensities of the preedge peaks are related to the local structures surrounding the chromium atom in the compounds and provide useful information on the coordination number surrounding the chromium atom [14–16]. As shown in Fig. 4, the CrMS thin film exhibits an intense single preedge peak in the XANES spectrum, indicating that the chromium oxide moieties has a tetrahedral coordination. Fig. 5 shows the FT-EXAFS spectrum of the sample and the data are given without corrections for phase shifts. The CrMS thin film exhibits only a strong peak at around 1.6 Å (uncorrected for the phase shift) which can be assigned to the neighboring oxygen atoms (Cr=O and Cr–O bonds), indicating the presence of the chromium oxide moieties in the tetrahedrally coordination.

Fig. 6 shows the UV–vis absorption spectra of the Cr-containing non-porous silica films and Cr-containing mesoporous silica (CrMS) thin films with various chromium content. The absorption bands of these thin films are mainly observed in

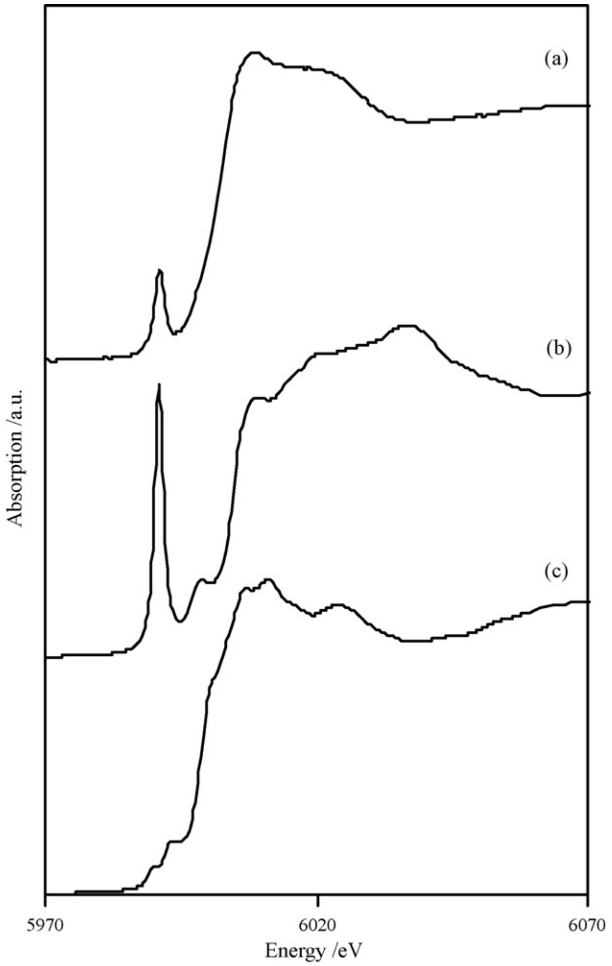

Fig. 4. XANES spectra of (a) Cr-containing mesoporous silica (CrMS) thin film (Cr/Si = 0.05); (b) K_2CrO_4; and (c) Cr_2O_3.

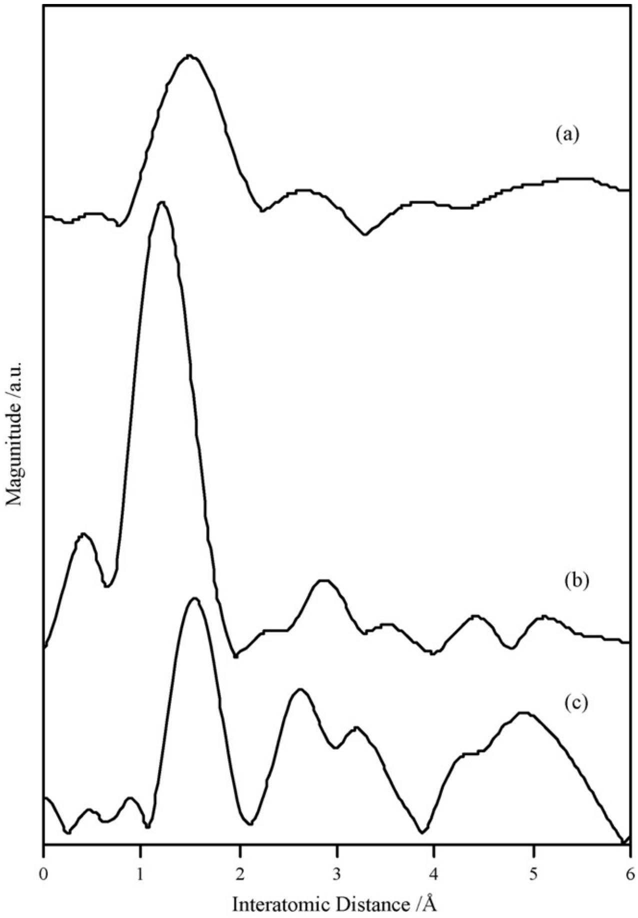

Fig. 5. FT-EXAFS spectra of (a) Cr-containing mesoporous silica (CrMS) thin film (Cr/Si = 0.05); (b) K_2CrO_4; and (c) Cr_2O_3.

the UV light wavelength region. The Cr-containing non-porous silica thin films exhibit the similar spectra. When the Cr/Si ratio of CrMS thin films becomes higher, the absorption bands at the region longer than 400 nm (visible-light region) can be observed more distinctly. This band can be assigned to the charge transfer from O^{2-} to Cr^{6+} of the tetrahedrally coordinated chromium oxide moieties [14–16]. The absorption bands assigned to the absorption of the dichromate of Cr_2O_3 cluster cannot be observed above 550 nm, indicating that tetrahedrally coordinated chromium oxide moieties exist. These results indicate the formation of the isolated and tetrahedrally coordinated chromium oxide moieties in these thin films. The presence of the isolated chromium oxide moieties was also confirmed by XAFS analysis.

3.2. Measurement of contact angle of water droplet

Fig. 7 shows the images of water droplets observed on the Cr-containing non-porous silica films, Cr-containing mesoporous silica (CrMS) thin film and CrMS thin film (Cr/Si = 0.05) after polymerization. The contact angle of water droplet observed on these samples before and after irradiation of UV light or visible light (interior lightning condition) is summarized in Fig. 8. The water contact angles on these CrMS thin films even before UV light irradiation were much smaller than Cr-containing non-porous silica films and CrMS thin films with Cr/Si = 0.1 having the distorted porous structure. After UV light irradiation, the water contact angle on the CrMS thin film become very small, while the water contact angle on Cr-containing non-porous silica film does make only small change. In the case of the CrMS thin film, the water contact angle becomes smaller even after visible light irradiation.

Fig. 9 summarizes the contact angle of water droplet observed after visible light irradiation (interior lightning condition) on the Cr-containing non-porous silica films, the mesoporous silica thin film without chromium, and Cr-containing mesoporous silica (CrMS) thin film with various chromium contents. The water contact angles on the CrMS thin are smaller than on the surface of Cr-containing non-porous silica films and the mesoporous silica thin film without chromium indicating that the presence of porous structure and isolated chromium oxide moieties are essential to realize the hydrophilic surface. These observations also indicate that the CrMS thin film can perform the super-hydrophilic property not only under UV light irradiation but also under visible light irradiation while in the previous study it was found that the

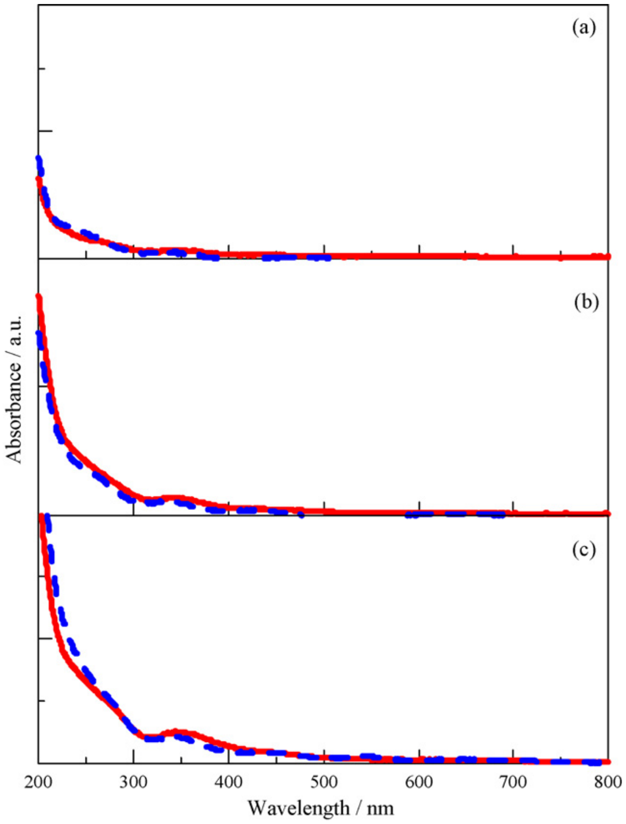

Fig. 6. UV–vis spectra of Cr-containing non-porous silica thin films (dotted line) and Cr-containing mesoporous silica (CrMS) thin films (solid line) with various Cr/Si ratios. (a) Cr/Si = 0.01; (b) 0.03; and (c) 0.05.

Ti-containing mesoporous silica thin film can perform only under UV light irradiation. The charge transfer excited state of the tetrahedrally coordinated chromium oxide moieties formed under UV light and visible light irradiation play a significant role in the photo-induced super-hydrophilic property.

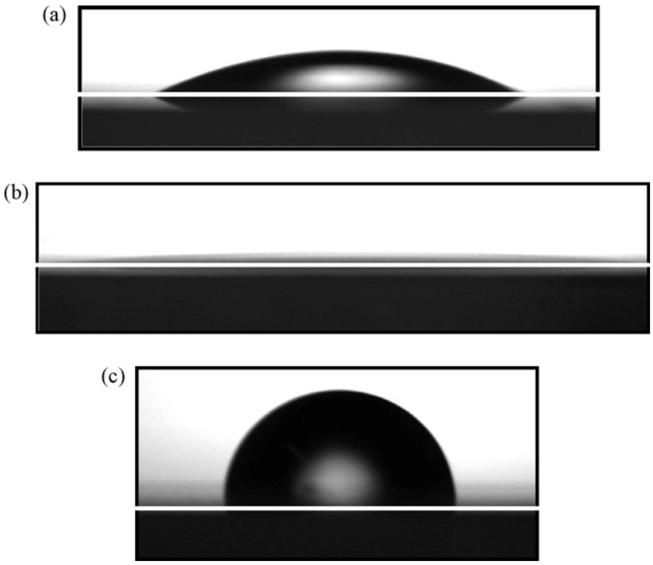

Fig. 7. The images of water droplets on (a) Cr-containing non-porous silica thin film and Cr-containing mesoporous silica (CrMS) thin films (b) before and (c) after polymerization.

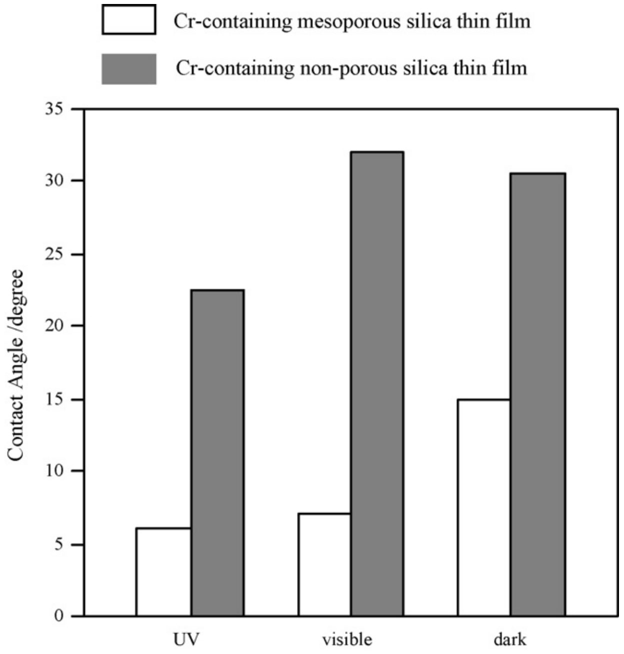

Fig. 8. Contact angles of water droplets on Cr-containing mesoporous silica (CrMS) and Cr-containing non-porous silica thin films (Cr/Si = 0.01) under UV light irradiation, interior lightning, and dark conditions.

3.3. Effect of ethylene polymerization over CMS thin films

Because the isolated tetrahedrally coordinated chromium oxide supported on silica is an industrially significant heterogeneous catalyst for ethylene polymerization [25,26],

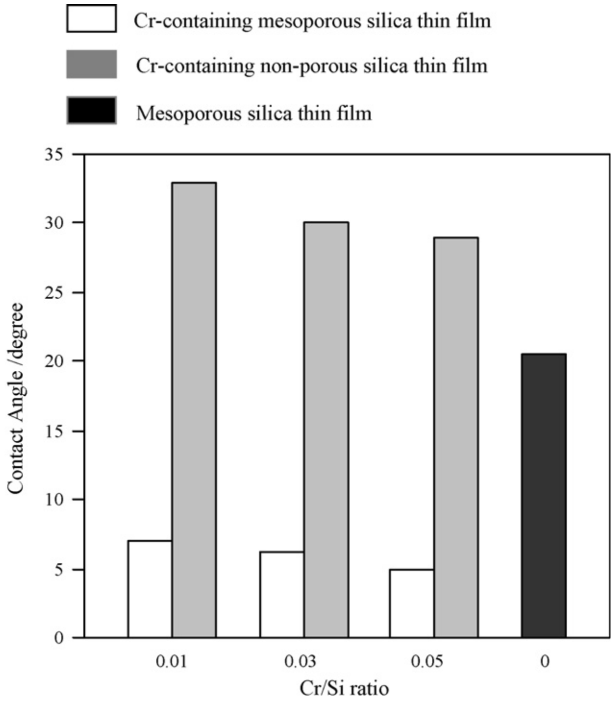

Fig. 9. Contact angles of water droplets on Cr-containing mesoporous silica (CrMS), Cr-containing non-porous silica thin film, and mesoporous silica thin films under interior lightning conditions.

it can be expected that the highly dispersed chromium oxide moieties in the Cr-containing mesoporous silica (CrMS) thin film can synthesize polyethylene from ethylene gas. The polymerization of ethylene on the CrMS thin film was carried out under UV light irradiation of sample in the presence of ethylene gas. Fig. 10 shows the IR spectra on the CrMS thin film observed after UV light irradiation for ethylene polymerization [14,15,27]. On the CrMS thin film after UV light irradiation the two strong bands at 2854 cm^{-1} and 2916 cm^{-1} assigned to symmetric and antisymmetric stretching modes of CH_2 groups and a weak peak at 2955 cm^{-1} assigned to stretching vibration of terminal CH_3 group are observed indicating the formation of polyethylene. As shown in Fig. 2, the CrMS thin films can keep its transparency even after ethylene polymerization. Formation of polyethylene is also observed by the FE-SEM photo images of on the CrMS thin film (Cr/Si = 0.05) after polymerization as shown in Fig. 3. The polyethylene synthesized on the CrMS thin film was well-fixed on the substrate.

Fig. 7 also shows the images of water droplets on the CrMS thin film after polymerization. The contact angle of water droplets observed on the CrMS thin films is also shown in Fig. 11. The water contact angle of the sample after polymerization increased greatly to be much larger than the angle observed on the original one. This observation apparently indicates that the tetrahedrally coordinated chromium oxide moieties play a role to synthesis of polyethylene on the surface of the CrMS thin film and can convert the surface property of the thin film from hydrophilic to hydrophobic.

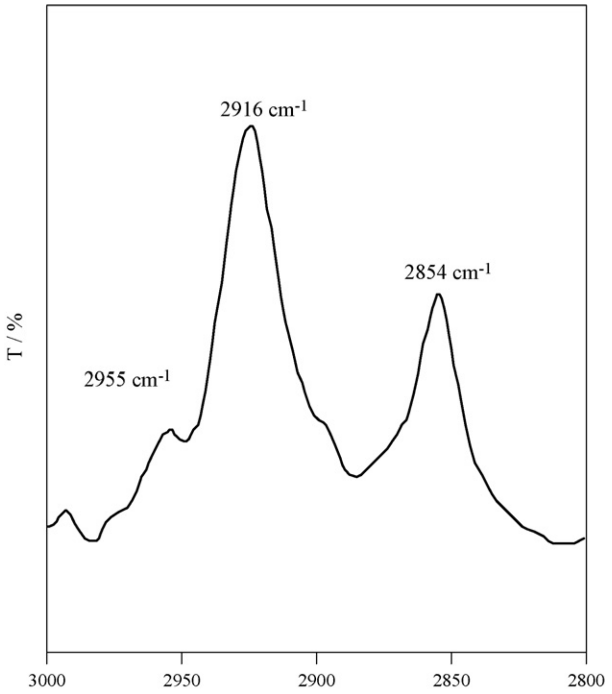

Fig. 10. IR spectrum of the Cr-containing mesoporous silica (CrMS) thin film after polymerization of ethylene.

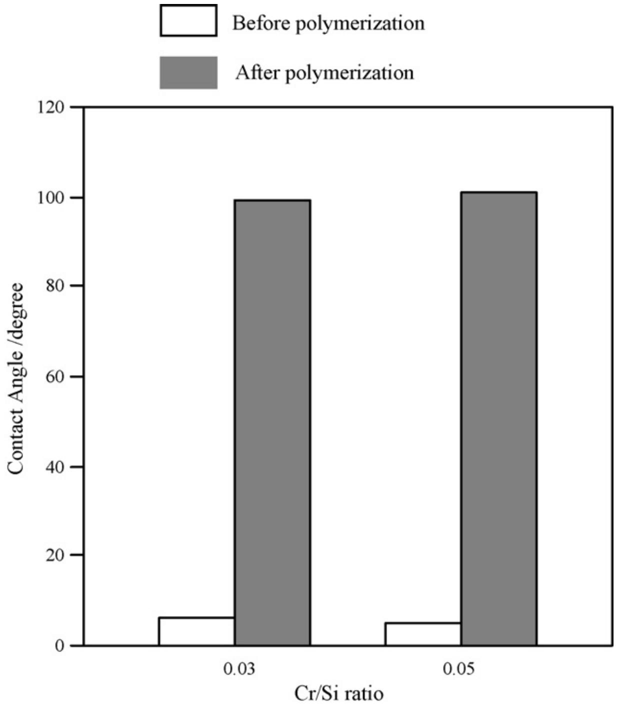

Fig. 11. Contact angles of water droplets on Cr-containing mesoporous silica (CrMS) thin films before and after polymerization.

4. Conclusion

Using the sol–gel/spin-coating method with polyoxyethylene(4)lauryl ether (Brij^{R} 30) as surfactant, the transparent Cr-containing mesoporous silica (CrMS) thin films can be prepared on the quartz plate. With Cr/Si ratio of 0.01–0.05, the chromium oxide moieties were present as a tetrahedrally coordinated Cr-oxide moiety in these thin films. These CrMS thin films have demonstrated a strong hydrophilic surface property even before UV irradiation. The CrMS thin film exhibited the photo-induced super-hydrophilic property not only under UV light irradiation but also under visible light irradiation. Furthermore, the CrMS thin film has demonstrated a photo-polymerization ability on its surface under UV light irradiation. This polymer formation can convert the surface property of CrMS thin film from hydrophilic to hydrophobic.

Acknowledgements

This work was supported by the Grant-in-Aid for Scientific Research (KAKENHI) from the Ministry of Education, Culture, Sports, Science, and Technology (Grants 17360388). This work is also partly performed under the project of collaborative research at the Joining and Welding Research Institute (JWRI) of Osaka University. The X-ray adsorption experiments were performed at the Photon Factory of KEK (2007G031, 2007G077) with helpful advice from Prof. M. Nomura and Prof. Y. Inada.

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