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Characterization of self-standing Ti-containing porous silica thin films and their reactivity for the photocatalytic reduction of CO_2 with H_2O

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Abstract

Self-standing porous silica thin films with different pore structures were synthesized by a solvent evaporation method and used as photocatalysts for the photocatalytic reduction of CO_2 with H_2O at 323 K. UV irradiation of these Ti-containing porous silica thin films in the presence of CO_2 and H_2O led to the formation of CH_4 and CH_3OH as well as CO and O_2 as minor products. Such thin films having hexagonal pore structure exhibited higher photocatalytic reactivity than the Ti-MCM-41 powder catalyst even with the same pore structure. From FTIR investigations, it was found that these Ti-containing porous silica thin films had different concentrations of surface OH groups and showed different adsorption properties for the H_2O molecules toward the catalyst surface. Furthermore, the concentration of the surface OH groups was found to play a role in the selectivity for the formation of CH_3OH. © 2002 Published by Elsevier Science B.V.

Keywords: Porous thin film; Ti-oxide; Photocatalyst; Reduction of CO_2; CH_3OH

1. Introduction

Photocatalysis for the reduction of CO_2 with H_2O is of interest not only as a reaction system utilizing artificial photosynthesis but as a way to use carbon sources for the synthesis of hydrocarbons and oxygenates such as CH_4 and CH_3OH. Various fundamental studies in the photocatalytic reduction of CO_2 on highly active titanium oxides have been carried out [1–8] and we have already reported that the charge transfer excited complexes $[Ti^{3+}–O^{-}]^*$ of the tetrahedrally coordinated titanium oxide can work as a photocatalyst for the reduction of CO_2 with H_2O [9–17]. In this reaction, CO_2 and H_2O molecules are competitively activated by the charge transfer excited complexes to form CH_3OH, CH_4 and CO. We have found that the values of the H_2O/CO_2 ratio influence the selectivity for the formation of these products.

In the syntheses of zeolites and mesoporous molecular sieves, the morphology of these materials was mainly in powdered form. However, powdered material systems are difficult to handle for practical use as photocatalysts. Therefore, the synthesis of transparent porous silica thin films such as zeolite films is a subject of current interest [18–21]. These transparent porous silica thin films have a larger surface area, in contrast to metal oxide thin films on a quartz substrate, and can realize the efficient absorption of light,

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showing that they have potential for use as effective photocatalysts.

In the present study, self-standing Ti-containing mesoporous silica thin films with two different mesostructures were synthesized by a solvent evaporation method and their reactivities for the photocatalytic reduction of CO_2 with H_2O to produce CH_4 and CH_3OH at 323 K was investigated. We have focused on the effects of the morphology of the photocatalysts on the photocatalytic reactivity as well as on the relationship between the concentration of the surface OH groups of the catalysts and the selectivity for the formation of CH_3OH.

2. Experimental

Ti-containing porous silica thin films with different pore structures and Ti contents were synthesized by a solvent evaporation method [20–22]. Ti-PS(h, 25) and Ti-PS(c, 50), in this text, showed hexagonal and cubic structure with a Si/Ti ratio of 25 and 50 for the pore structures, respectively. A typical synthetic procedure for the self-standing films is as follows: tetramethoxysilane (abbreviated as TMOS), vinyltrimethoxysilane (VTMOS) (TMOS:VTMOS = 7:1), titanium-tetra(iso-propoxide) (TPOT), octadecyltrimethyl-ammonium chloride (C_{18}TAC) and methanol ((TMOS + VTMOS):TPOT:C_{18}TAC = 1:1/50 or 1/25:1/8) were mixed by magnetic stirring and then allowed to react under acidic conditions by the addition of HCl for 10 min at room temperature. In order to hydrolyze the alkoxides, deionized water was added to the mixture. When the water/Si ratio was 1/3 and 4/3, Ti-PS(h, x) (x = Si/Ti ratio) and Ti-PS(c, 50) were synthesized, respectively. The resulting solution was then deposited on a poly(ethylene) film and dried in air at 333 K for 1 day to remove the solvent and complete the condensation of the alkoxides. The dried films were then peeled off from the substrate and flexible self-standing transparent films were obtained.

The photocatalytic reduction of CO_2 with H_2O was carried out with the catalysts (50 mg) in a quartz cell with a flat bottom (88 cm^3) connected to a conventional vacuum system (10^{-4} Pa range). Prior to photoreactions and spectroscopic measurements, the catalysts were heated in O_2 at 723 K for 8 h, and evacuated at 473 K for 2 h. UV irradiation of the catalysts in the presence of CO_2 (36 μmol) and gaseous H_2O (180 μmol) was carried out using a 100 W high-pressure Hg lamp at 323 K. The reaction products collected in the gas phase were analyzed by gas chromatography. The number of incident photons to the cell was determined by means of a potassium ferrioxalate actinometer. The difference between the number of photons passing through the Ti-containing porous silica thin films and the corresponding number with the pure silica thin films can provide the number of photons absorbed by the Ti-oxide catalysts. Thus, the quantum yield for the photocatalytic reduction of CO_2 with H_2O to produce CH_4 and CH_3OH could be determined.

The XRD patterns were obtained on a RAD IB diffractometer (Rigaku) using monochromatic Cu Kα radiation operated at 30 kV and 30 mA. The self-standing films were placed on a glass substrate for the XRD measurements. The UV absorption spectra were recorded with a Shimadzu UV-2200A photospectrometer. The XAFS spectra were measured at the BL-9A facility [23] of the Photon Factory at the National Laboratory for High Energy Physics, Tsukuba. The Ti K-edge absorption spectra were recorded in the fluorescence mode at 298 K. The photoluminescence spectra of the catalysts were measured at 77 K using a SPEX FLUOLOG-3 spectrophotofluorometer. The FTIR spectra were recorded at 298 K with a JASCO FTIR-7300 spectrometer.

3. Results and discussion

The XRD patterns of the Ti-containing porous silica thin films suggested that Ti-PS(h, x) and Ti-PS (c, 50) have the pores of hexagonal and cubic structures, respectively. These XRD patterns were in good agreement with those of the porous silica thin films shown in previous literature [19–21].

Fig. 1 shows the UV–Vis absorption spectra of the Ti-containing porous silica thin films. Ti-PS(h, 50) and Ti-PS(c, 50) exhibit an absorption band in the wavelength region of 200–260 nm, attributed to the ligand-to-metal charge transfer (LMCT) band of the highly dispersed tetrahedrally coordinated titanium oxide species [24,31]. On the other hand, the Ti-PS(h, 25) shows an absorption band in the wavelength region of 250–340 nm as well as the LMCT band, indicating

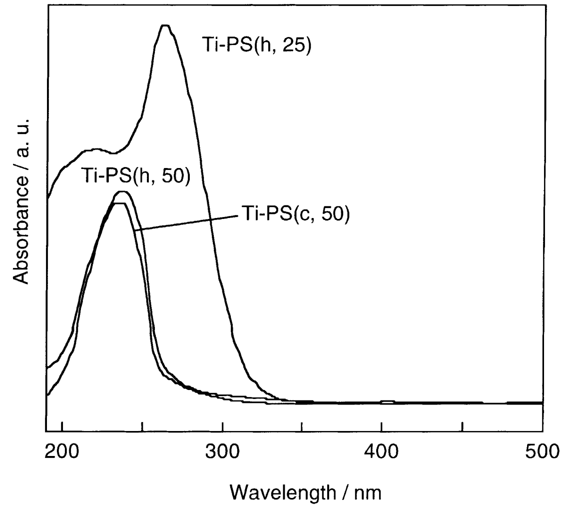

Fig. 1. The UV–Vis absorption spectra of the Ti-containing porous silica thin films.

the presence of two kinds of titanium oxide species, i.e., a tetrahedrally coordinated titanium oxide species and an aggregated octahedrally coordinated titanium oxide species.

Fig. 2 shows the XANES spectra of the Ti-containing porous silica thin films. The XANES spectra of the Ti-containing compounds at the Ti K-edge show several well-defined preedge peaks that can be attributed to the local structures surrounding the Ti atoms [25–27]. These relative intensities of the preedge peaks provide useful information on the coordination number surrounding the Ti atom. As shown in Fig. 2, both Ti-PS(h, 50) and Ti-PS(c, 50) exhibit an intense single preedge peak. Because tetrahedrally coordinated Ti such as $Ti(OPr^i)_4$ was found to exhibit an intense single preedge peak due to the lack of an inversion center in the regular tetrahedron structure [25,33], the observation of this intense single preedge peak indicates that the titanium oxide species in the Ti-containing porous silica thin films has a tetrahedral coordination. Ti-PS(h, 50) and Ti-PS(c, 50) exhibit preedge peaks having the same intensities and positions, indicating that both Ti-containing porous silica thin films have the same titanium coordination. Ti-PS(h, 25) shows lower preedge intensity as compared with the other Ti-containing porous silica thin films and a shift to higher energy level of the edge position, indicating the presence of both a tetrahedrally coordinated titanium oxide species and an octahedrally coordinated titanium oxide species [25].

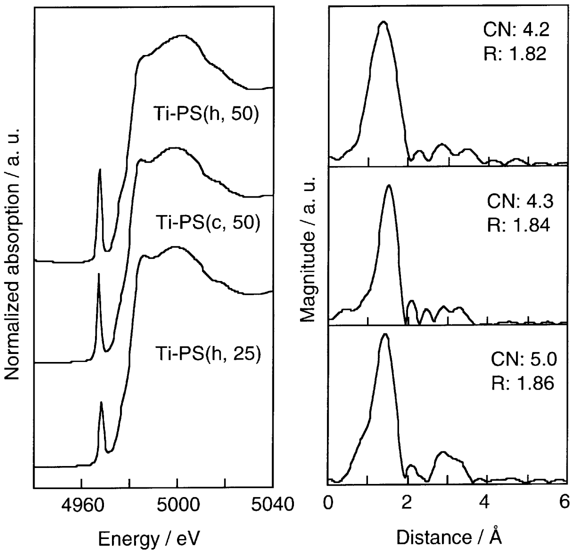

Fig. 2. Ti K-edge XANES (left) and FT-EXAFS (right) spectra of the Ti-containing porous silica thin films. CN, coordination number and R, Ti–O bond distance (Å).

From the curve fitting analysis of the EXAFS spectra, it was found that the titanium oxide species of Ti-PS(h, 50) and Ti-PS(c, 50) exists in tetrahedral coordination with an atomic distance of 1.82 and 1.84 Å, respectively. The coordination number and Ti–O bond distances of Ti-PS(h, 25) are 5.0 and 1.86 Å, indicating the presence of an aggregated octahedrally coordinated titanium oxide species as well as the tetrahedrally coordinated titanium oxide species. These results are in good agreement with the results obtained from UV–Vis absorption investigations.

Fig. 3 shows that Ti-containing porous silica thin films (Ti-PS(h, 50)) exhibit a photoluminescence spectrum at around 485 nm by excitation at 260 nm at 77 K. The observed photoluminescence and absorption bands are in good agreement with those previously observed with the highly dispersed tetrahedrally coordinated titanium oxides prepared in silica matrices [28–36]. We can, therefore, conclude that the observed photoluminescence spectrum is attributed to the radiative decay process from the charge transfer excited state to the ground state of the highly dispersed titanium oxide species in tetrahedral coordination.

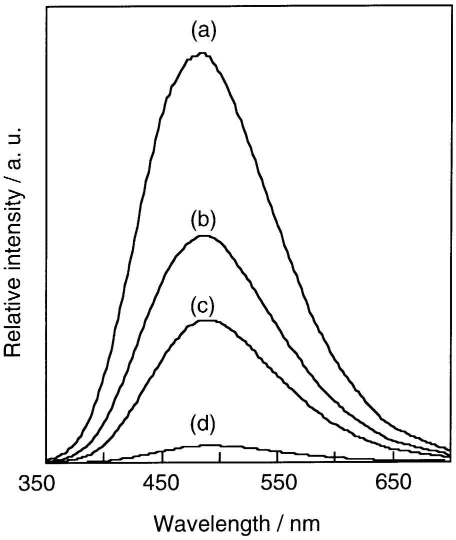

Fig. 3. The photoluminescence spectrum of the Ti-containing porous silica thin film (Ti-PS(h, 50)) (a) and the effect of the addition of CO_2 and H_2O molecules on the photoluminescence spectrum at 77 K. Excitation at 260 nm. The amount of the addition of CO_2: (b) 0.15, H_2O: (c) 0.15, (d) 1.5 mmol per g of catalyst.

As shown in Fig. 3, the addition of H_2O or CO_2 molecules onto the Ti-containing porous silica thin film leads to an efficient quenching of the photoluminescence. The lifetime of the charge transfer excited state was also found to be shortened by the addition of CO_2 or H_2O, its extent depending on the amount of added gasses. Such an efficient quenching of the photoluminescence with CO_2 or H_2O suggests not only that the tetrahedrally coordinated titanium oxide species locates at positions accessible to the added CO_2 or H_2O but also that the added CO_2 or H_2O interacts and/or reacts with the titanium oxide species in both its ground and excited states. On the other hand, as shown in Fig. 4, the photoluminescence of the Ti-containing porous silica thin film with Si/Ti = 25 shows peaks at around 485 and 510 nm by excitation of 260 and 280 nm, respectively. From the UV–Vis and XAFS investigations, the peak at around 510 nm can be attributed to the photoluminescence of the aggregated octahedrally coordinated titanium oxide species.

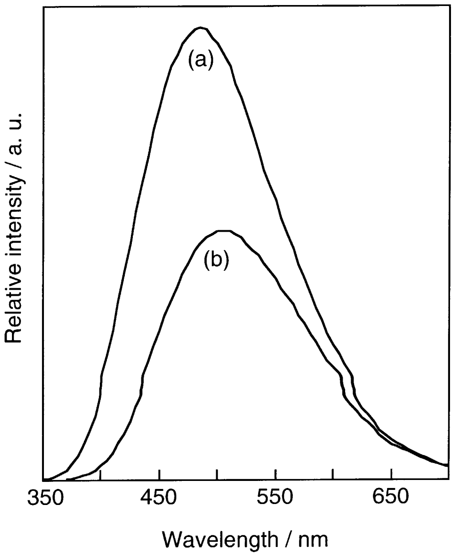

Fig. 4. The photoluminescence spectrum of Ti-PS(h, 25) at 77 K. (a) Excitation at 260 nm, (b) excitation at 280 nm.

Fig. 5 shows the Stern–Volmer plots for the yields of the photoluminescence using the steady state treatment for Eq. (1)

$$\frac{\Phi_0}{\Phi} = 1 + \tau k_q[Q] \qquad (1)$$

where Φ_0 and Φ are the yields of the photoluminescence in the absence and presence of quencher molecules, respectively. τ, k_q and $[Q]$ represent the lifetime of the excited triplet state, the quenching rate constant, i.e., the reaction rate constant of the charge transfer excited complexes toward the quencher molecules and the concentration of the quencher molecules on the surface, respectively. In the case of the same lifetimes, the reactivity of the reactant molecules toward the photo-active sites depends on the values of k_q. However, in the present case, the reactivity of the reactant molecules can be compared with the slopes of Stern–Volmer plots since the lifetimes of the excited state of the titanium oxide for these catalysts are different. As shown in Fig. 5, the slopes of the Stern–Volmer plots of the photoluminescence quenching by the addition of CO_2 and H_2O for Ti-PS(h, 50) are higher than those for Ti-PS (c, 50). CO_2 and H_2O molecules, thus, interact more efficiently with the charge transfer excited complexes of Ti-PS(h, 50). Moreover, as shown in Fig. 6, the slopes of the Stern–Volmer plots for the addition

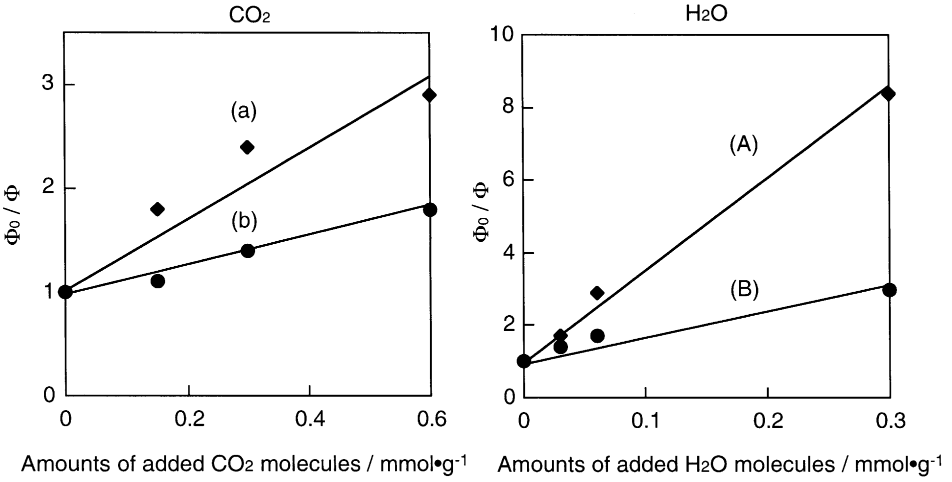

Fig. 5. Stern–Volmer plots of Φ_0/Φ values versus [Q] for the yields of the photoluminescence for CO_2 (a, b) or H_2O (A, B) on Ti-PS (h, 50) (a, A) and Ti-PS(c, 50) (b, B).

of CO_2 and H_2O for the emitting species observed at around 480 nm are higher than those for 510 nm. However, with the Stern–Volmer plots for the addition of the H_2O molecules, the difference in slopes between the two emitting species is small. These results indicate that the titanium oxide species of the Ti-PS(h, 50) and Ti-PS(h, 25) lead to selective interaction with H_2O molecules under the conditions of competitive adsorption of the CO_2 and H_2O molecules.

UV irradiation of the Ti-containing porous silica thin film photocatalysts in the presence of CO_2 and H_2O led to the formation of CH_4 and CH_3OH as the main products. As shown in Fig. 7, the rates of these photoformed products increase linearly against the UV irradiation time and the secondary reaction of these products were not detected under dark conditions nor with UV irradiation of the mesoporous silica thin films without titanium oxides. These results

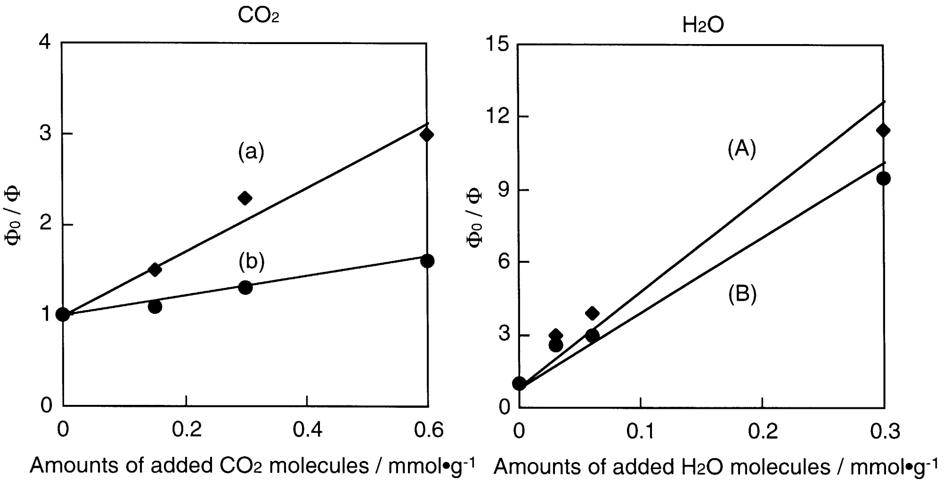

Fig. 6. Stern–Volmer plots of Φ_0/Φ values versus [Q] for the yields of the photoluminescence for CO_2 (a, b) or H_2O (A, B) on Ti-PS (h, 25). (a, A) Excitation at 260 nm, (b, B) excitation at 280 nm.

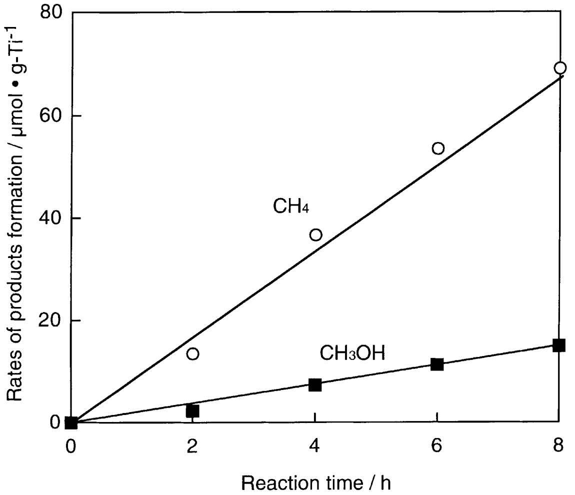

Fig. 7. Reaction time profiles of the photocatalytic reduction of CO_2 (36 μmol) with H_2O (180 μmol) to produce CH_4 and CH_3OH on the Ti-containing porous silica thin film photocatalyst.

clearly indicate that the presence of both titanium oxides included within the mesoporous silica framework as well as UV irradiation are indispensable for the photocatalytic reduction of CO_2 with H_2O to take place on the catalysts. Fig. 8 shows the product distribution in the photocatalytic reduction of CO_2 with H_2O on the Ti-containing porous silica thin film catalysts. Ti-PS(h, 50) exhibits higher photocatalytic reactivity than the powdered Ti-MCM-41 even with the same pore structure. Moreover, the catalyst ground to powder form, Ti-PS(h, 50), maintains higher photocatalytic reactivity as compared with the powdered Ti-MCM-41. These results indicate that the high photocatalytic reactivity of Ti-PS(h, 50) is attributed to the efficient absorption of UV light due to its high transparency. Ti-PS(h, 25) involving an aggregated titanium oxide species exhibits the formation of CH_4 as with the case of the bulk TiO_2 catalyst. Ti-PS (c, 50) shows higher selectivity for the formation of CH_3OH, though its photocatalytic reactivity is lower than that of Ti-PS(h, 50).

In powdered form, the effect of the scattering of light on the particle surface would be large so that effective light absorption and measurement may not be realized. It is, therefore, a great advantage to use transparent Ti-containing porous silica thin film photocatalysts to measure the exact quantum yield of the photocatalytic reaction using chemical actinometers. Fig. 9 shows the quantum yield of the Ti-containing porous silica thin films and the titanium oxides anchored onto the porous silica glass (PVG), i.e.,

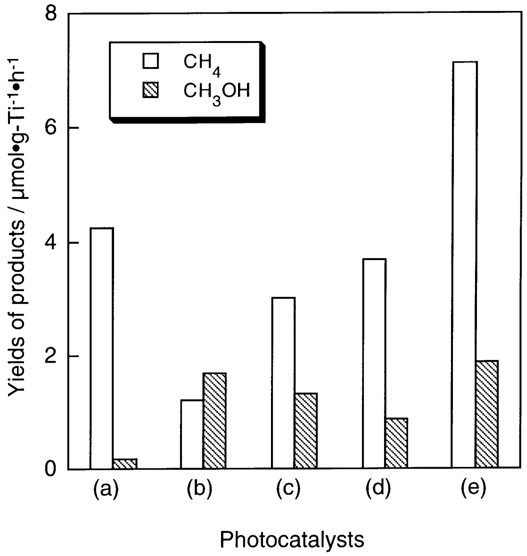

Fig. 8. Yields of CH_4 and CH_3OH in the photocatalytic reduction of CO_2 with H_2O on Ti-PS(h, 25) (a), Ti-PS(c, 50) (b), Ti-MCM-41 (c), the powdered form of Ti-PS(h, 50) (d) and Ti-PS(h, 50) (e). Reaction time is 6 h and intensity of light is 265 μW cm^{-2}.

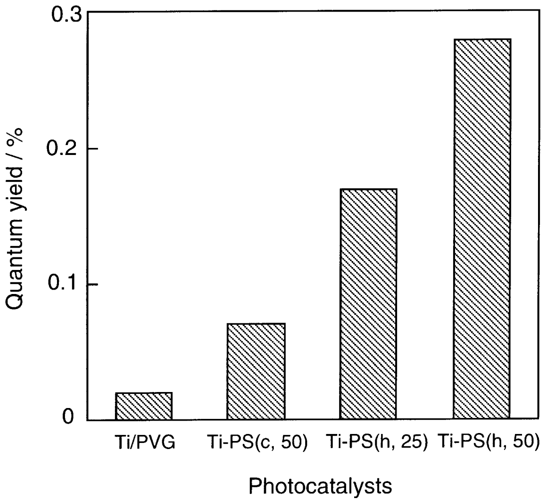

Fig. 9. The quantum yields of the Ti-containing porous silica thin films and the titanium oxides anchored onto the transparent porous silica glass (PVG), Ti/PVG.

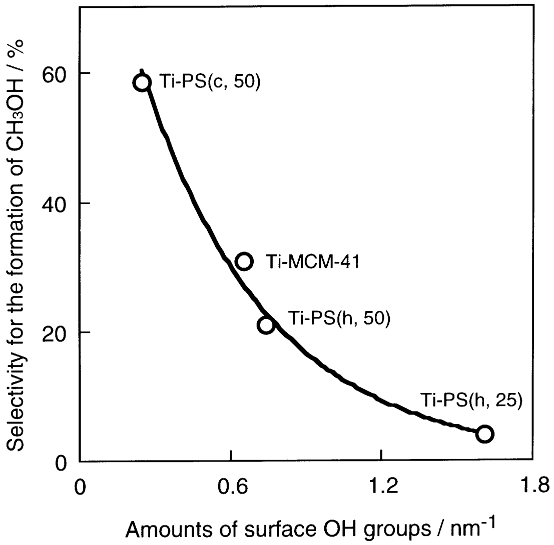

Fig. 10. The relationship between the selectivity for the formation of CH_3OH and the amount of surface OH groups.

Ti/PVG. As shown in Fig. 9, in contrast to the quantum yield observed with transparent Ti/PVG, the quantum yields observed with transparent Ti-containing porous silica thin films have improved remarkably. Such improvement in the reactivity can be attributed to the larger surface area and higher transparency of the Ti-containing porous silica thin films as compared with Ti/PVG. These results clearly suggest that the photocatalytic reactivity of the transparent Ti-containing porous silica thin films is quite high and sufficiently effective for utilization in functional photocatalytic systems.

Fig. 10 shows the relationship between the selectivity for the formation of CH_3OH and the amount of the surface OH groups. As shown in Fig. 10, Ti-containing porous silica thin films having small amounts of surface OH groups exhibit the highest selectivity for the formation of CH_3OH. In general, large amounts of H_2O molecules can adsorb on the surface of the catalysts having a high concentration of surface OH groups. It can, therefore, be assumed that the relative concentration of the H_2O molecules surrounding the tetrahedrally coordinated titanium oxide species influence the selectivity for the formation of CH_3OH. As shown in the Stern–Volmer plots, H_2O molecules can easily interact with the excited state of the titanium oxide species in the case of catalysts having larger amounts of surface OH groups. In a previous study, in the case of high values for the H_2O/CO_2 ratio, the selectivity for the formation of CH_4 became higher [9]. These results indicate that in the case of high concentrations of surface OH groups, the formation of CH_4 occurred mainly due to the high concentration of the H_2O molecules surrounding the tetrahedrally coordinated titanium oxide species and the easy interaction of the H_2O molecules with the excited state of the titanium oxide species. In the case of a low concentration of surface OH groups, the selectivity for the formation of CH_3OH may be higher since the reaction for the formation of CH_4 is blocked. Moreover, in the case of catalyst systems having both aggregated octahedrally coordinated titanium oxide species and a high concentration of surface OH groups, these two main factors are the characteristic reactivity of bulk TiO_2 toward the formation of CH_4 and the easy interaction of the H_2O molecules affect the selectivity in this reaction.

4. Conclusions

It was found that Ti-containing porous silica thin film photocatalysts exhibited higher photocatalytic reactivity than the powdered Ti-MCM-41 photocatalyst. These Ti-containing porous silica thin films exhibited high quantum yields, and their high reactivity could be attributed to their high transparency. It was found that these thin films having a high transparency are good candidates as efficient photocatalysts for various significant reactions. Moreover, the amount of surface OH groups was related to the selectivity in the photocatalytic reduction of CO_2 with H_2O. Photocatalysts having small amounts of surface OH groups showed high selectivity for the formation of CH_3OH.

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