Photocatalytic reduction of CO_2 with H_2O on Ti-containing porous silica thin film photocatalysts

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Two different Ti-containing porous silica thin films having a hexagonal and cubic pore structure were synthesized and used as photocatalysts for the reduction of CO_2 with H_2O at 323 K. UV irradiation of the 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 with a high quantum yield of 0.28%. These porous silica thin film photocatalysts having a hexagonal pore structure exhibited higher reactivity than the Ti-MCM-41 powder photocatalysts with the same pore structure.

KEY WORDS: mesoporous thin film; reduction of CO_2; photocatalyst; formation of CH_3OH; quantum yield.

1. Introduction

The photocatalytic reduction of CO_2 with H_2O is of interest, not only as a reaction system utilizing artificial photosynthesis, but also as a way to use carbon sources for the synthesis of hydrocarbons and oxygenates such as CH_4 and CH_3OH. In the past few years, a large number of studies have been conducted on the photocatalytic reduction of CO_2 with H_2O on various semiconductor photocatalysts [1–6]. In particular, titanium oxide photocatalysts have attracted much attention due to their high reactivity and stability. Pioneering and fundamental studies in the photocatalytic reduction of CO_2 with H_2O were carried out by Anpo and Chiba [7] on highly active titanium oxides having a tetrahedral coordination, and since then we have reported that the UV irradiation of Ti-MCM-41 and Ti-MCM-48 mesoporous systems in the presence of CO_2 and H_2O at 323 K also leads to the formation of CH_4 and CH_3OH [8–10]. We have found that the highly dispersed tetrahedrally coordinated titanium oxide species incorporated in the mesoporous silica matrix of MCM-41 and MCM-48 shows higher reactivity and selectivity for the formation of CH_3OH as compared with small particle TiO_2 semiconducting materials. However, powdered material systems such as Ti-MCM-41 and Ti-MCM-48 are difficult to handle for practical use. Recently, porous silica materials with various morphologies such as for films, hollow and hard spheres, as well as fibers, have been synthesized [11–15]. Among these, an ideal morphology would be films for applications as a photocatalyst due to their high transparency.

In the present study, self-standing Ti-containing mesoporous silica thin films with two different mesostructures were synthesized by a solvent evaporation method [16] and their reactivity for the photocatalytic reduction of CO_2 with H_2O to produce CH_4 and CH_3OH at 323 K has been investigated.

2. Experimental

Ti-containing porous silica thin films were synthesized by a solvent evaporation method, as has been reported in a previous work [16]. A typical synthetic procedure for the self-standing films is as follows: tetramethoxysilane (TMOS), vinyltrimethoxysilane (VTMOS) (TMOS : VTMOS = 7 : 1), TPOT (tetraisopropylorthotitanate), C_{18}TAC (octadecyltrimethylammonium chloride), and methanol [(TMOS + VTMOS) : TPOT : C_{18}TAC : methanol = 1 : 1/50 (or 1/25) : 1/8 : 1/25] were mixed by magnetic stirring and the mixture was 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(x) (x = Si/Ti ratio) and Ti-PS(c) were synthesized, respectively. The resulting solution was then deposited on poly(ethylene) film and dried in air at 333 K for 24 h to remove the solvent and to complete condensation of the alkoxides. The dried films could then be peeled off from the substrate and flexible self-standing transparent films were obtained.

Prior to photoreactions and spectroscopic measurements, the catalysts (50 mg) were heated in O_2 at 723 K for 8 h and then evacuated at 475 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

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high-pressure Hg lamp (Toshiba SHL 100 W, λ > 250 nm) for 6 h 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 gives 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 was determined. The amounts of the surface OH groups were estimated from the amounts of the eliminated OH groups as H_2O during the evacuation of the catalyst in the temperature ranges from 573 to 1073 K, by monitoring the decrease in the surface OH groups with the IR peak at around 3740 cm^{-1}. The Ti content in the synthesized thin films was confirmed to be much closer to the Ti content in the original starting precursor gel by atomic absorption analysis. The BET surface areas of these Ti-containing porous silica thin films were ~900 $m^2\,g^{-1}$.

3. Results and discussion

Figure 1 shows the XRD patterns of Ti-containing porous silica thin film. As shown in figure 1(a) and 1(b), the XRD patterns of Ti-PS(25) and Ti-PS(50) indicate two diffraction peaks assigned to (100) and (200) reflections of hexagonal symmetry. When compared with that of powdered samples, no (110) reflection could be observed on the films. This is attributed to the fact that the channel axis is oriented parallel to the film plane [17]. The XRD pattern of Ti-PS(c) shows three diffraction peaks assigned to (200), (210) and (211) of cubic symmetry. These structures were also confirmed by TEM images.

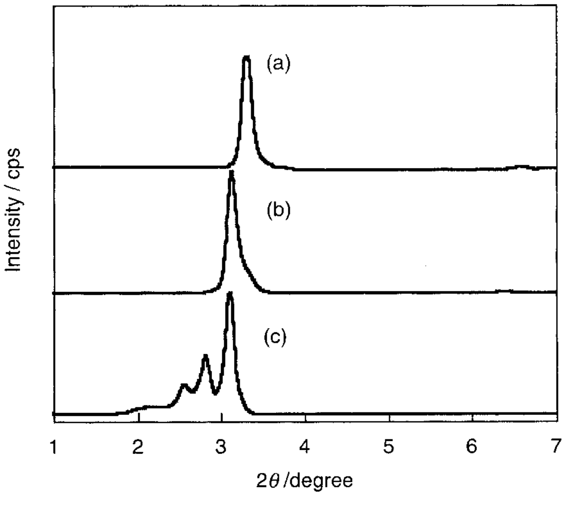

Figure 1. The XRD patterns of Ti-containing porous silica thin films (a) Ti-PS(25), (b) Ti-PS(50) and (c) Ti-PS(c).

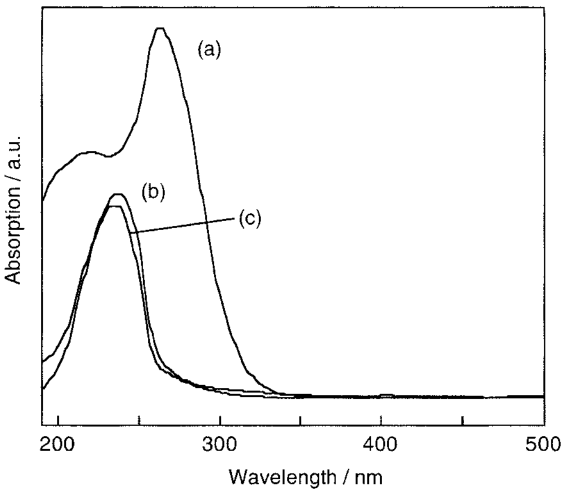

Figure 2. UV–vis absorption spectra of Ti-containing porous silica thin films (a) Ti-PS(25), (b) Ti-PS(50) and (c) Ti-PS(c).

Figure 2 shows the UV–vis absorption spectra of Ti-containing porous silica thin films. Ti-PS(50) and Ti-PS(c) both exhibit an absorption band in the wavelength region of 200–270 nm, attributed to the LMCT (ligand-to-metal charge transfer) band of the highly dispersed tetrahedrally coordinated titanium oxide [18]. The Ti-PS(25) shows an absorption band in the wavelength region of 250–340 nm as well as the LMCT band, indicating the presence of two kinds of titanium oxide species, *i.e.* tetrahedrally coordinated titanium oxide species and aggregated octahedrally coordinated titanium oxide species.

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 figure 3, the yields of these photoformed products increase linearly against the UV irradiation time, while these reaction products were not

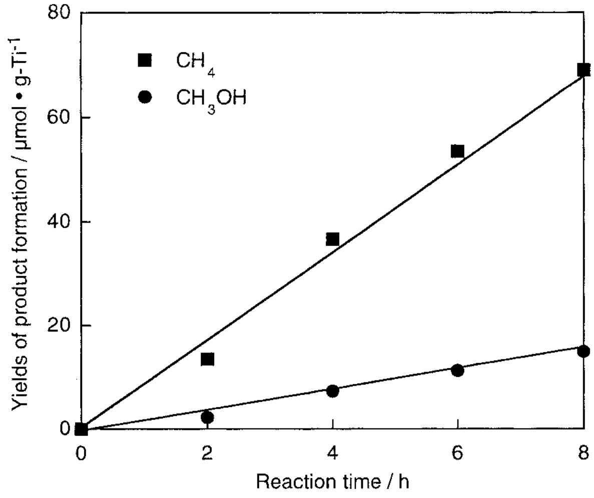

Figure 3. Reaction time profiles of the photocatalytic reduction of CO_2 (36 µmol) with H_2O (180 µmol) to produce (a) CH_4 and (b) CH_3OH on a Ti-containing porous silica thin film photocatalyst.

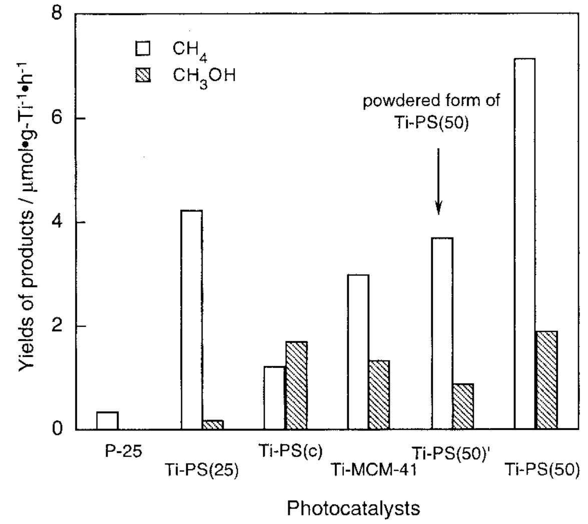

Figure 4. Yields of CH_4 and CH_3OH in the photocatalytic reduction of CO_2 with H_2O on Ti-containing porous silica thin film photocatalysts. Reaction time is 6 h. Intensity of light is 265 μW cm^{-2}.

detected under dark conditions nor with UV irradiation of mesoporous silica thin films without titanium oxides. These results clearly indicate that both the presence of titanium oxide 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.

Figure 4 shows the product distribution in the photocatalytic reduction of CO_2 with H_2O on Ti-containing porous silica thin film catalysts. Ti-PS(25) having an aggregated titanium oxide species mainly leads to the evolution of CH_4. These results are similar to those for the widely used TiO_2 (P-25) catalysts. Ti-PS(c) shows higher selectivity for the formation of CH_3OH, though the photocatalytic reactivity was lower than that of the Ti-PS(50) catalyst. Among these Ti-containing porous silica thin films, Ti-PS(50) shows the highest apparent photocatalytic reactivity per gram of Ti. Moreover, Ti-PS(50) exhibits two times higher reactivity as compared with powdered Ti-MCM-41 having a hexagonal pore structure, and the photocatalytic reactivity is highest among all of the catalysts which were investigated. It was found that the catalyst ground to powdered form, Ti-PS(50)′, maintains higher reactivity as compared with Ti-MCM-41. In powdered form, it can be expected that the effect of the scattering of light on the particle surface would be large and effective light absorption could, therefore, not be realized to measure. Therefore, it is of great benefit to use transparent Ti-PS(50) thin film photocatalyst to measure the exact quantum yield of the photocatalytic reaction using chemical actinometers. The quantum yield of Ti-PS(50) for the formation of CH_4 and CH_3OH from CO_2 and H_2O was determined to be 0.28%. In contrast to the value obtained with the titanium oxides anchored on transparent porous silica glass (PVG), Ti/PVG, (quantum yield was 0.02%), the quantum yield obtained with transparent Ti-PS(50) thin film photocatalyst has been improved remarkably. Such improvement in the reactivity is attributed to larger surface area and higher transparency of Ti-containing porous silica thin films as compared with that of Ti/PVG. These results clearly suggest that the photocatalytic reactivity of transparent Ti-PS(50) thin films is quite high and has enough reactivity for the utilization of these thin films for the real photocatalytic systems.

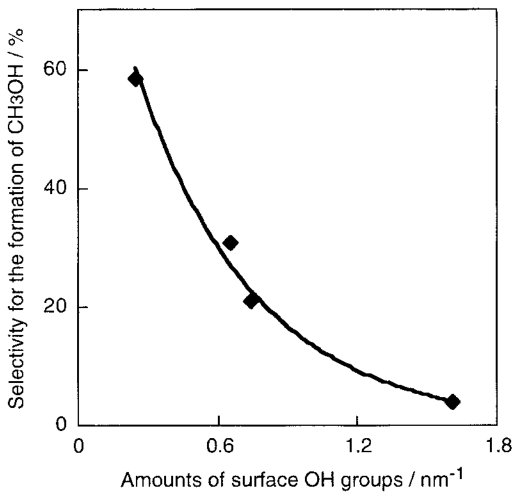

Figure 5. The relationship between the selectivity for the formation of CH_3OH and the amount of surface OH groups.

Figure 5 shows the relationship between the selectivity for the formation of CH_3OH and the amounts of the surface OH groups. As shown in figure 5, 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 absorb on the surface of the catalysts having high concentrations of surface OH groups due to the hydrogen interaction between the H_2O molecules and silanols. It is thus considered that the relative concentration of the H_2O molecules surrounding the tetrahedrally coordinated titanium oxide species influences the selectivity in the photocatalytic reduction of CO_2 with H_2O. 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 becomes higher. Therefore, in the case of high concentrations of surface OH groups, the formation of CH_4 occurred mainly due to the high concentration of H_2O molecules surrounding the tetrahedrally coordinated titanium oxide species. In the case of low concentrations of surface OH groups, the selectivity for the formation of CH_3OH may be higher because the reaction for the formation of CH_4 was prevented.

4. Conclusions

Ti-containing porous transparent silica thin film photocatalysts exhibited higher reactivity than powdered

Ti-MCM-41 photocatalysts, and the quantum yield for the photocatalytic reaction of CO_2 with H_2O to produce CH_4 and CH_3OH was determined to be 0.28% at 323 K. These results clearly indicated that Ti-containing porous thin films having high transparency are good candidates as efficient photocatalysts. Moreover, it was found that the amounts of surface OH groups were closely related to the selectivity for the formation of CH_3OH in the photocatalytic reduction of CO_2 with H_2O.

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