Synthesis of Ti-containing Porous Silica with High Photocatalytic Activity

Katsunori Kosuge* and Puyam S. Singh#
Materials Processing Department, National Institute for Resources and Environment, 16-3 Onogawa, Tsukuba, Ibaraki 305-8569

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Ti-containing mesoporous silica with high photocatalytic activity has been synthesized by a simple reaction system at ambient temperature; one of these products shows photocatalytic activity in the decomposition of acetic acid as high as 39 times than that of one of most photocatalytic commercial anatase.

A variety of Ti-containing mesoporous materials, having high surface areas, high pore volumes such as Ti-MCM-41, Ti-HMS and Ti-MCM-48, have been developed in recent years.[1] However, there are only few reports[2] on the photocatalytic activity of these materials although titania anatase phase has been known as good photocatalyst.[3] Here we report synthesis of photocatalytically active Ti-containing porous silica by modifying our earlier synthesis approach[4] to obtain mesoporous silica using tetraethylorthosilicate (TEOS), tetraethylorthotitanate (TEOT), octylamine and HCl aq without any extra solvent such as alcohols in the conventional procedures.[5] A typical procedure for the synthesis is as follows: The solution of TEOS and TEOT was stirred for 15 minutes, and then mixed with octylamine in a molar ratio of 1:0.4, followed by addition of HCl aq. (the molar ratio of octylamine to tetraethylorthosilicate was 1:1.7). The mixture was then stirred for 24 h. The solid products were separated by centrifugation, dried at 50 °C for 2 days and finally calcined over 500 °C for 2 h or, 900 °C for 1 h to yield photocatalytically active porous material. The porous products are designated as MTSO or MTSO(x)-T, where x and T are the Ti mol% and calcination temperature, respectively. Photocatalytic activity of MTSO was evaluated by examining the decomposition of acetic acid. A 0.5 g of the sample was dispersed in a 400 ml of aqueous acetic acid with 2.66 mM of the concentration and irradiated with a 120 W low-pressure Hg lamp at room temperature. After 1 h, the concentration of remaining acetic acid was determined by TOC (total organic carbon) analyzer.

Figure 1(i) shows the powder X-ray diffraction (XRD) patterns of MTSO(2) and MTSO(9) samples calcined at 500 °C for 2 h and 900 °C for 1 h. Both products calcined at 500 °C exhibit a single diffraction peak corresponding to interplanar spacing of ca. 3.6 nm. Higher order Bragg reflections are not observed. These commonality of their diagnostic XRD pattern are usually observed in mesoporous materials such as HMS [5] and MSU-1[6], indicating that MTSO has poorly ordered mesostructure. Calcination at 900 °C results in the decrease or loss of this reflection at low angel due to the destruction of the mesostructure of MTSO. Though low intensity of anatase phase was detected in the MTSO(x>7), the intensity of this phase does not increase with increasing calcination temperature without no observation of transformation from anatase to rutile phase. This implies that Ti sites are still in anatase phase but react with SiO_2 in the framework accompanied by the destruction of the mesostructures. On the other hand, no existence of anatase phase for MTSO upto 5.62 mol% Ti and their calcined samples even at 1000 °C indicated well dispersed titanium in the silicate framework. From the analytical results for N_2 adsorption-desorption isotherms, the porous properties of MTSO such as BET surface area (S_{BET}), pore diameter and pore volume are given in Table 1. With increasing Ti content, S_{BET} slightly decreases and pore size distribution become broader while little change of mean pore diameter is observed. Though S_{BET} remarkably decrease upon calcination at 900 °C the products still exhibit relatively high surface areas and pore volumes. However the clear pore size distribution curves were not given by the conventional analytical methods such as HK[8] and DH plot[9], indicating that the products have no uniform pores and wide range of pore size distribution. The incorporation of Ti into the silicate framework is evaluated by UV-vis diffuse reflectance spectroscopy. Figure 1(ii) shows UV-vis spectra of MTSO under ambient conditions along with those of TS-1 and anatase.

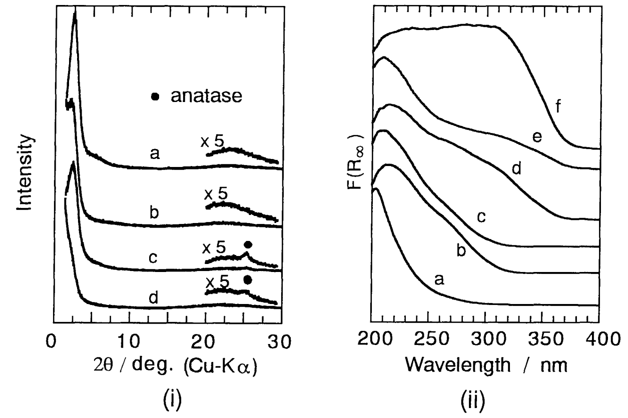

Figure 1. (i) X-ray diffraction patterns of (a) MTSO(2)-500, (b) MTSO(2)-900, (c) MTSO(9)-500, (d) MTSO(9)-900. (ii) UV-vis spectra of (a) TS-1, (b) MTSO(2)-500, (c) MTSO(2)-900, (d) MTSO(9)-500, (e) MTSO(9)-900, and (f) anatase.

Table 1. Properties of Ti-containing mesoporous silica prepared by ambient temperature synthesis

MTSO(x)-T x and T / °C	Ti content / mol %	S_{BET} / $m^2 g^{-1}$	V / ml g^{-1}	D / nm
2 (500)	1.57	919	0.61	2.3
2 (900)	1.57	613	0.33	nd
6 (500)	5.62	909	0.66	2.2
7 (500)	6.98	907	0.66	2.2
9 (500)	9.41	881	0.59	2.2
9 (900)	9.41	449	0.22	nd

nd = not determined. S_{BET},V, and D represent BET surface area, mesopore volume, and mean pore diameter. These values are determined by t-plot method[7]. The data in parentheses are temperature at which the samples were calcined in air. Ti and Si were determined by ICP method on Perkin Elmer, Optima 3000.

MTSO(2) gives the band centered at 220 nm and 260 nm as a shoulder, of which patterns are very similar to those of other mesoporous Ti-containing materials[1,5,10] such as Ti-MCM-41and Ti-HMS with the same level Ti-content. MTSO(9) exhibits the band in the 300-330 nm besides the band at 220 nm. In addition, a slight blue shift at ca.210-220 nm and decrease of the band at ca.260-270 nm are observed with increase of calcination temperature. It is well known that the absorption band at 210 nm for TS-1 and broad band centered at 310 nm for anatase are characteristic for the tetracoordinated and octahedracoordinated Ti, respectively.[1,11] The band at 260-270 nm can be attributed to the presence of Ti atoms in 5-, and 6-fold coordinations which are most likely generated through hydration of the tetrahedrally coordinated sites with tetrahedral coordination being in the majority.[12] Stone et al.[13] recently found striking similarity in the UV-vis. spectra of locally amorphous titania mesoporous material and crystalline anatase phase, except that the UV absorption threshold was sharper in crystalline titania compared to those of locally amorphous titania mesoporous materials. Therefore, the observed blue shift at 210-220 nm and sharper intensity in the UV-vis. spectra of MTSO calcined at 900 °C is the indication of more locally ordered Ti-sites in silicate framework than that of MTSO calcined at 500 °C. No band around 320 nm was observed in the calcined samples MTSO(x<7). On the other hand, MTSO(9) is found to have a extraframework Ti as anatase phase in addition to tetracoordinated framework Ti, which is consistent with the results in XRD patterns.

The main consequence of the synthesis by the incorporation of titanium into mesoporous silica should be a potential catalytic activity.[1,14] Figure 2 compares the photocatalytic activity per 1mol Ti of MTSO materials with that of ST-01, one of most active photocatalytic anatase produced by Ishihara Techno Co. Ltd. As shown in the Figure 2 MTSO(2) calcined at 900 °C is very active which is as high as 39 times than that of ST-01. Recently it has been pointed out that highly dispersed tetrahedral titanium exhibits unique and efficient photocatalytic activity.[15] Higher titanium content of MTSO shows lower activity in comparison with that of low titanium content, but still much active than that of ST-01. The decrease in activity at higher Ti content might be from less Ti dispersion in silicate framework. Furthermore, it has been proposed that the bulk defects, surface defects are detrimental factors for lowering photocatalytic activity and has been suggested that materials to be partially crystallized prior to use as a photocatalyst.[13] The variety of microenvironments of Ti-sites within the porous materials therefore, may account for these features. The observed high activity of MTSO, calcined at 900 °C might be resulted from the combination of less bulk and surface defects and more locally ordered Ti-sites in silicate framework than that of MTSO calcined at 500 °C. This is in agreement with the observed sharper UV absorption threshold of MTSO at 900 °C than that of MTSO at 500 °C.

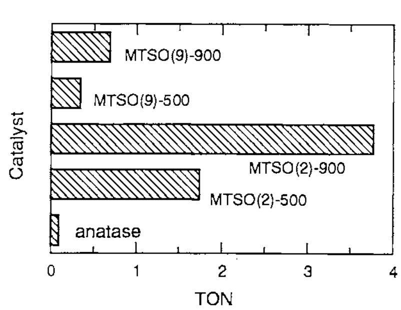

Figure 2. Photocatalytic activity for acetic acid on various MTSO and anatase. TON means the number of moles of acetic acid converted per one mole of Ti.

In conclusion, the simple synthesis of Ti-containing mesoporous silica of which Si^{4+} be isomorphously substituted by Ti^{4+} in the silicate framework upto ca.5 mol%, is reported. The calcined products show the higher photocatalytic activity than that of one of most photocatalytic commercial anatase in the decomposition of aqueous acetic acid. Further study will be required to obtain deeper evaluation for these photocatalytic properties.

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