Preparation of Mesoporous TiO_2 Photocatalyst by Selective Dissolving of Titania–Silica Binary Oxides

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Mesoporous TiO_2 photocatalyst, which consisted of uniform mesopores (pore size about 4 nm) and with anatase framework and huge surface area as high as 329 $m^2\ g^{-1}$, was prepared by selectively dissolving of silica in Ti–Si binary oxides.

Since M41S was first demonstrated in 1992,[1] the use of surfactants and amphiphilic block copolymers to organize mesoporous structures has been extended to the preparation of non-silica mesoporous metal oxides.[2–5] Antonelli et al. reported synthesis of mesoporous titania by template agents, and obtained mesoporous titania with amorphous framework.[6,7] It has been illustrated that the photocatalytic activity of amorphous titania was negligible,[8] thus, mesoporous TiO_2 prepared by templating approach with amorphous framework is not suitable to be used as high-efficiency photocatalyst. Most nanocrystalline titania really exhibited high photocatalytic properties in photocatalytic reactions using suspensions of powdered TiO_2,[9] however the separation of TiO_2 nanocrystals from water is difficult[10] and recent research has focussed on the preparation of active immobilized photocatalysts for water treatment at the cost of lowering of the photocatalytic activity. Titania-silica binary oxides are intriguing catalysts and catalyst supports since their surface reactivities depend strongly on composition and homogeneity of mixing.[11] Most Ti–Si binary oxides with low ratio of Ti to Si show high catalytic activity. Here, we describe a novel method for preparation mesoporous TiO_2 without templating agents. This mesoporous TiO_2 with crystalline framework and huge surface area was prepared by selectively dissolving (SD) of silica in titania–silica binary oxides.

The silica/titania binary oxides were prepared by the sol–gel technique according to the following procedures. To 138 mL of a 1:1 (v/v) tetraethyl orthosilicate (TEOS) ethanol solution was added 5.4 mL of 0.1 M HNO_3. This solution was refluxed at 343 K for 2 h, and cooled to room temperature as the stock silica sol (sol A). Then 207 mL of a 1:1 (v/v) tetrabutyl orthotitanate (TBOT)–ethanol solution was added dropwise into 36 mL of sol A with stirring. The mixture was stirred for 1 h at room temperature, and 12.2 mL of 0.1 M HNO_3 mixed with 25 mL of ethanol was slowly added. Thus, the final molar ratio of water to the sum of Ti and Si was adjusted to 2. After gelation, the composite gel was dried at 383 K for 24 h, ground in a mortar, then sieved to a particle size finer than 100 μm, and finally calcined at temperatures higher than 873 K for 4 h to improve the crystallinity of titania. The calcined binary oxides were treated with 2.5–10 M NaOH solution with stirring for 12 h at 333 K. Then the precipitate was washed by distilled water until pH < 7, and dried at 383 K for 24 h. After SD removal of amorphous silica, the network occupied previously by silica was open-porous continuously now.

Sol–gel processes for the preparation of Ti–Si mixed oxides are plagued by TiO_2 domain formation,[12] which leads to undesirable phase segregation. The pre-hydrolyzing of TEOS is crucial to obtain homogeneous texture of silica/titania mixed oxides. For preparation of silica/titania binary oxide with the molar ratio of Ti to Si higher than 8:2, some amount of acetylacetone (acac) as stabilizer has to be added into TBOT solution. In the absence of acac, gel formation was disfavored due to the rapid precipitation of oxide–alkoxide aggregates. The crystallization of amorphous titania in composites into anatase, antatase–rutile transformation and particle size of anatase nanocrystals depended closely on the contents of silica. For instance, at the molar ratio of Ti:Si = 9:1, amorphous titania transformed into anatase, anatase transformed into rutile at about 773 K and 1073 K, respectively; and the particle size of remaining anatase in sample $9TiO_2{\cdot}SiO_2$ calcined at 1073 K was 16.6 nm. In the binary oxide with the molar ratio of Ti:Si = 1:3 or less, no rutile phase could be detected by XRD and particle size of anatase was only 6.5 nm even after calcined at 1273 K for 2 h, which was much finer than that in titania-silica composites at higher molar ratio of Ti to Si. The pure titania transformed into rutile phase and with particle size larger than 200 nm after calcined at 1073 K for 4 h. These results illustrated the uniform network of silica was thermally robust enough and prevented anatase TiO_2 particles in the binary oxide from the growing and transforming effectively.

Titania/silica mixed oxides with Ti:Si = 9:1 after calcining at 973 K for 4 h, had specific surface area of 3.5 $m^2\ g^{-1}$, suggested it was sintered. The resulting mesoporous TiO_2 (M-TiO_2) obtained by alkaline treatment of the binary oxides has an effective BET surface area of 329.0 $m^2\ g^{-1}$ and a pore volume of 0.33 $cm^3\ g^{-1}$. The surface area was raised about 100 times after SD treatment and 98% of silica in the binary oxides was removed. Different batches of M-TiO_2 were prepared by SD method, and all exhibited mesoporous nature independent of the composition of binary oxides. The surface areas of M-TiO_2 batches obtained from $9TiO_2{\cdot}SiO_2$ were in the range of 315.2 to 332.7 $m^2\ g^{-1}$. The type IV N_2 adsorption–desorption isotherms in Figure 1 clearly illustrate the mesoporous nature of M-TiO_2. The inserted pore size distribution of M-TiO_2 shows most pore size of 4 nm in diameter and some micropores (< 2 nm) also existed in M-TiO_2. When M-TiO_2 was heated at 673 K for 2 h, its surface area decreased to 133.5 $m^2\ g^{-1}$. It still kept a high surface area (101.7 $m^2\ g^{-1}$) even when heated at 773 K for 2 h, while micropores collapsed in this sample.

The particle morphology of M-TiO_2 is wormholed and predominated by ca. 5 μm particles, as shown by scanning electron microscopy (SEM, Figure 2a). Shown in Figure 2b is the transmission electron microscopy (TEM) image of M-TiO_2 as

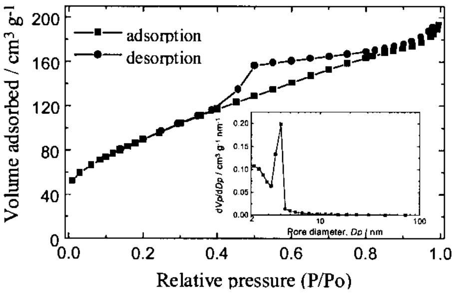

Figure 1 N_2 adsorption–desorption isotherm and BJH pore size distribution plot (inset) of the sample mesoporous TiO_2. It was prepared by alkaline treatment of the binary oxides $9TiO_2{\cdot}SiO_2$ calcined at 973 K for 4 h.

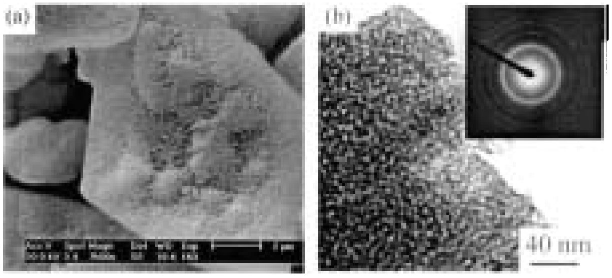

Figure 2 SEM and TEM images of mesoporous TiO_2 obtained by SD treatment of Si–Ti oxides in 10 M NaOH solution.

described in Figure1. TEM revealed that after selectively dissolving of silica in titania-silica oxides, highly packed, random pores appear throughout the aggregates. The corresponding pore sizes are estimated to be in the 2.0–4.0 nm range, which are consistent with those determined form BJH desorption isotherms in Figure 1. The inserted electron patterns in Figure 2b indicated the wall of M-TiO_2 was in the anatase phase. The primary particle size of titania was 8.7 nm, calculated from XRD peak broadening, which was also in agreement with TEM observation.

To test the photocatalytic activity, the removal of chromate, a toxic and carcinogenic pollutant in water, was investigated. High-pressure mercury lamp with the strongest emission at wavelength 365 nm as the irradiation source, the initial concentration of Cr^{VI} was 8.62×10^{-4} M, and the concentration of photocatalyst was 2.0 g L^{-1}, respectively. It is well known that upon UV irradiation crystalline titania catalyzes chromium(VI) to chromium(III).[13,14] As shown in Figure 3, in the reduction of chromate to chromium(III), the photocatalytic activity of $9TiO_2{\cdot}SiO_2$ is negligible. The photocatalytic activity of mesoporous TiO_2 was much higher than that of composite oxides such as $TiO_2{\cdot}9SiO_2$ with surface area of 306 $m^2\,g^{-1}$ and comparable to anatase TiO_2 nanoparticles in size of 10.5 nm. Its photocatalytic activities could be enhanced significantly by deposition of elementary platinum clusters on TiO_2 surface.[15] Platinum deposits are believed to cause better separation of photogenerated charge carriers, with electrons being collected in platinum islands. However, the separation Pt/TiO_2 from aqueous medium and its recycling are crucial to practical manipulation and recovery Pt anions since Pt is very rare and expensive. After removal of the product species of chromium(III) by 1 M H_2SO_4 solution, both M-TiO_2 and Pt/M-TiO_2 keep similar surface area and photocatalytic activity as the fresh one does in this reaction.

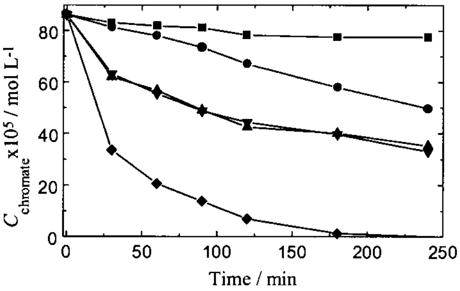

Figure 3 Photocatalytic reduction profiles of chromium(VI) to chromium(III) on (■) $9TiO_2{\cdot}SiO_2$ after calcined at 973 K for 4 h, (●) $1TiO_2{\cdot}9iO_2$ after calcined at 873 K for 4 h with surface area of 306 m^2 g^{-1}, (▲) anatase TiO_2 nanoparticles in size of 10.5 nm, (▼)M–TiO_2 and (◆) 0.22 wt % Pt loaded on M–TiO_2.

In conclusion, a new class of mesoporous TiO_2 photocatalysts based on selectively dissolving of silica–titania composite oxides was introduced, and its characteristics were demonstrated. These mesoporous photocatalysts, with crystalline framework (anatase) and uniform pore size of 4 nm, had advantages over TiO_2 nanoparticles: they are easily separated from aqueous and recyclable keeping photocatalytic activity comparable to TiO_2 nanoparticles. They can be modified by photocatalytic deposition of noble metal, and the mesopores are taken as cages to keep noble metal islands on TiO_2 surface from deprivation. This strategy is also to be applied to synthesize other transit metal oxides powders and mesoporous films those are insoluble in alkaline aqueous solution.

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15 Pt was deposited on mesoporous TiO_2 by the photocatalytic reduction of H_2PtCl_6 solution in the mesoporous TiO_2 slurry. The particle size of Pt cluster was ca. 2–4 nm by TEM obsevation, and the amount of elementary Pt was 0.22 wt%, measured by Philips PW2400 X-ray fluorescence spectrometry (XRF).