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Preparation of TiO_2/SiO_2 hollow spheres and their activity in methylene blue photodecomposition

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Abstract−PSA [poly-(styrene-methyl acrylic acid)] latex particle has been taken into account as template material in SiO_2 hollow spheres preparation. TiO_2-doped SiO_2 hollow spheres were obtained by using the appropriate amount of $Ti(SO_4)_2$ solution on SiO_2 hollow spheres. The photodecomposition of the MB (methylene blue) was evaluated on these TiO_2-doped SiO_2 hollow spheres under UV light irradiation. The catalyst samples were characterized by XRD, UV-DRS, SEM and BET. A TiO_2-doped SiO_2 hollow sphere has shown higher surface area in comparison with pure TiO_2 hollow spheres. The 40 wt% TiO_2-doped SiO_2 hollow sphere has been found as the most active catalyst compared with the others in the process of photodecomposition of MB (methylene blue). The BET surface area of this sample was found to be 377.6 m^2g^{-1}. The photodegradation rate of MB using the TiO_2-doped SiO_2 catalyst was much higher than that of pure TiO_2 hollow spheres.

Key words: Hollow Sphere, TiO_2 Doped SiO_2, Photocatalyst, UV Irradiation, Methylene Blue

INTRODUCTION

Inorganic hollow spheres have increasingly attracted interest because of their potential applications in contaminated waste removal, catalysis, controlled delivery, medical imaging, artificial cells, light fillers, low dielectric constant materials, acoustic insulation and photonic crystals [1,2]. In recent years, synthesis of hollow spherical structured inorganic materials by using polymer templates has proven to be very successful. Hollow spheres already have been prepared by many researchers using different methods like controlling hydrolysis of alkoxide [4] or layer-by-layer coating [3] on uniform-sized template. In these methods, core-shell particles were separated from solution and the entire core template was removed by calcining them in air [5,6].

TiO_2 is now getting remarkable attention due to its excellent photocatalytic properties and become very popular in different processes as well as in various products also, such as pigments in food stuffs, paint and cosmetics, for its broad functionality, long-term stability and non-toxicity. Moreover, the oxidizing power of the photogenerated holes in TiO_2 has been proved to be successful in removing the pollutants from water and air by decomposing them [7].

Recently, Titania-silica mixed oxides have been attracting considerable attention. They are now widely used in acid catalysis, oxidation catalysis and photocatalysts. Among the many applications of this material, the most extensively studied area is photocatalysis, which is associated with the effect of support and quantum size. There are various industries, which produce mostly organic pollutants containing effluent water. The textile dyeing and finishing industry is a typical example. Appreciable amount of reactive azo remains in the waste water. To solve this problem, extensive study on photocatalytic degradation of pollutants had been attempted with more eco-friendly basis. Hsien et al. [8] has already prepared TiO_2 supported mesoporous MCM-41 using impregnation method. They found good photocatalytic activity during degradation of aromatic pollutants like benzene, monochlorobenzene, dichlorobenzene and phenol. Actually in titania-silica catalysts, TiO_2 was often dispersed on the silica surface to promote the catalytic activity by generating new acidic sites on Ti-O-Si bond.

In this study, we have succeeded in preparing SiO_2 hollow spheres by using poly-(styrene-methyl acrylic acid) latex particles as template. TiO_2-doped SiO_2 hollow spheres of various compositions were obtained by coating the SiO_2 particles with appropriate amount of $Ti(SO_4)_2$ solution. Special attention was directed to clarify how the photodecomposition process has been affected in various TiO_2 loaded samples, prepared under different conditions. The samples were then characterized by using XRD, UV-DRS, SEM and BET surface area analysis. Photocatalytic activity of the samples was evaluated by using the photodecomposition process of MB (methylene blue) under UV irradiation.

EXPERIMENTAL

In the present work, we have prepared pure SiO_2 hollow spheres by using the method as follows: 0.191 g of hexamethylenetetramine was first added into 35 ml of deionized water, followed by the addition of 0.98 ml of TEOS into them under vigorous stirring. Thereafter, 0.063 g of polystyrene particles and 1.98 ml of CTACl (cetyltrimethylammonium chloride) solution have been poured into the previously obtained solution. The mixture was aged at 70 °C for 12 h, and cooled to room temperature. The whole solution was then centrifuged to separate the particles and finally dried at 60 °C for 12 h. During the preparation of TiO_2 doped SiO_2 hollow sphere composite particles, the as-prepared SiO_2 hollow sphere particles were added into 35 ml of deionized water; followed by the addition of 0.8

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ml of HCl, 1.98 ml of CTACl and appropriate amount of $Ti(SO_4)_2$ solution. The remaining procedures were the same as conducted above during the preparation of SiO_2 hollow sphere particles. The obtained samples were then kept at 700 °C at a heating rate of 1 °C min^{-1} in air for 4 h for proper calcination. TiO_2-doped SiO_2 catalysts were prepared in various compositions and we have denoted the samples as the presence of Si in the particular catalyst. For example, 80% Si mean 80% SiO_2 in sample of 80%Si (TiO_2-SiO_2).

X-ray diffraction (XRD) patterns were measured on a Rigaku Denki (4057A2, Japan) diffractometer to detect the crystal phase composition of the prepared samples. Scanning electro microscope (SEM) images were obtained with a field emission scanning electron microscope (JSM-6400, Jeol). Optical properties of the samples were evaluated properly from a UV-diffuse reflectance spectrometer (V 650, Jasco). Surface area of the catalysts was evaluated by the Brunauer-Emmett-Teller (BET) method from nitrogen adsorption - desorption isotherms in a constant volume adsorption apparatus (ASAP 2010, Micrometrics).

The photocatalytic experiments were carried out by using a 6-W BLB lamp with a main emission peak at 365 nm, surrounded by a circulating water jacket for maintaining constant temperature during the reaction. The reaction suspensions were prepared by adding 0.05 g of photocatalyst powder into 300 ml of MB aqueous solution with an initial concentration of 13 mg l^{-1}; and after addition the total reaction system was continuously stirred for 1 h. The analytical samples were taken from the suspension and to remove the particles they were filtered through a 0.45 μm Milipore filter. We opted for the same method as in our previous paper [9]. The concentration of MB was measured by using a UV-vis spectrometer (V 650, Jasco) at 664 nm.

Table 1. BET surface area results of TiO_2-SiO_2 hollow sphere calcined at 700 °C

Sample	BET surface area (m^2g^{-1})
0%Si (TiO_2-SiO_2)	46.8
80%Si (TiO_2-SiO_2)	405.8
70%Si (TiO_2-SiO_2)	384.5
60%Si (TiO_2-SiO_2)	377.6

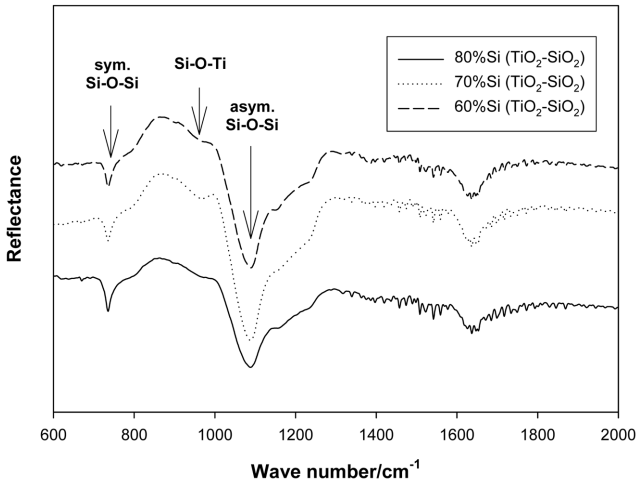
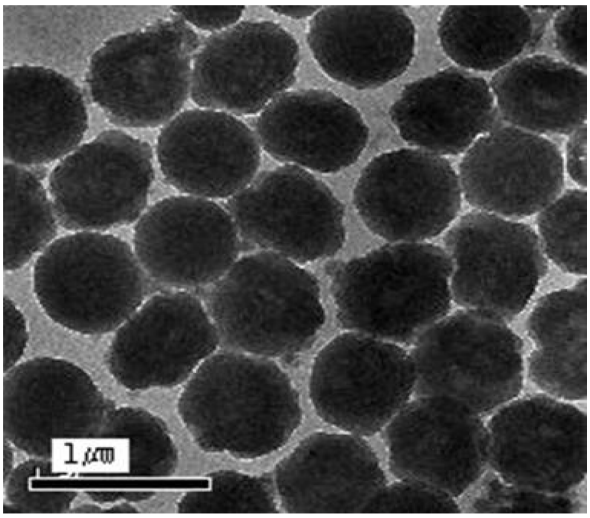
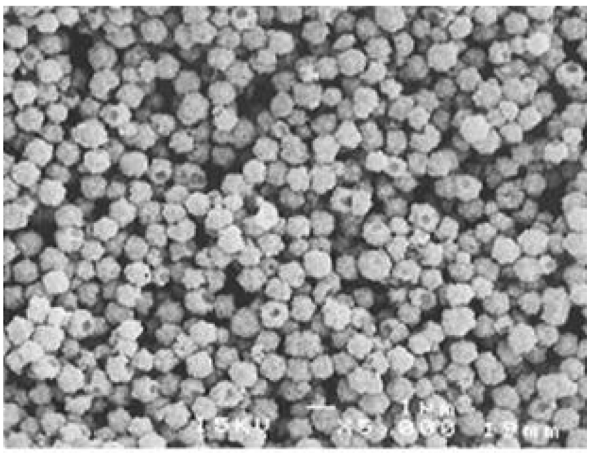


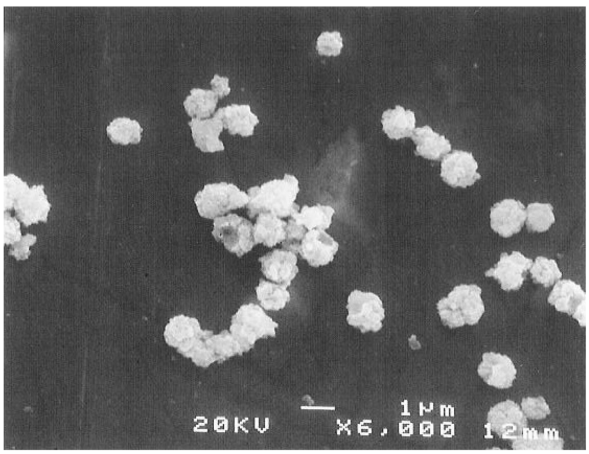
Fig. 1. FT-IR data of doped SiO_2 hollow spheres calcined at 700 °C with various Ti contents.



(A)



(B)



(C)

Fig. 2. TEM image of prepared PAS latex particles (A) and SEM images of TiO_2 hollow spheres calcined at 700 °C (B) and doped SiO_2 hollow spheres calcined at 700 °C with 40 wt% content (C).

RESULTS AND DISCUSSION

The specific surface area results of pure TiO_2 and TiO_2 doped SiO_2 hollow sphere particles are shown in Table 1. It is clear from the results that the pure TiO_2 hollow spheres showed very low surface area in comparison with those of prepared TiO_2 doped SiO_2 hollow spheres. At the same time, with increase of the TiO_2 loading in the doped samples the BET surface area value has been decreased. This may be due to partial occupation of the pores by TiO_2 species, which has been incorporated over the SiO_2 microspheres.

Fig. 1 illustrates the FT-IR data (range 600-2,000 cm^{-1}) for various TiO_2 doped SiO_2 hollow spheres. A distinguishing band at 1,085 cm^{-1} has appeared, which can be assigned to the asymmetric stretching frequency of Si-O-Si linkage. Another band around 790 cm^{-1} is also observed, which is ascribed to the symmetric vibration of Si-O-Si linkage, respectively. A band at 960 cm^{-1} corresponding to the asymmetric Si-O-Ti vibration [10] can be observed in all the samples. These results provide strong evidence that the incorporated TiO_2 particles have been structurally combined with SiO_2 particles, resulting in the formation of TiO_2-SiO_2 mixed oxides in all the catalysts.

Fig. 2(A), (B) and (C) shows the TEM and SEM images of prepared PAS latex particles, TiO_2 hollow spheres calcined at 700 °C and doped SiO_2 hollow spheres calcined at 700 °C with 40 wt% content, respectively. In our previous work, we prepared poly-(styrene-methyl acrylic acid) latex particles and TiO_2 hollow spheres. In Fig. 2(A) and 2(B), TEM image of PSA latex and SEM of pure TiO_2 hollow spheres are shown, respectively. The average diameter of PAS latex particles and pure TiO_2 hollow spheres was about 550 and 950 nm, respectively. It is clear from the diameter value that the size of the polymer spheres was smaller than that of prepared hollow spheres. It may be due to the slight particle aggregation of TiO_2 hollow spheres during the coating procedure.

The average diameter of TiO_2 doped SiO_2 hollow sphere was about 900-1,000 nm. The hollow structure reveals relatively uniformity when the TiO_2 loading is increased to 40 wt%, while it was diminished with the increase of Ti content in the catalyst. This implies that there was an appropriate amount of TiO_2 loading to form hollow sphere.

X-ray diffraction (XRD) patterns of mixed oxides of various Ti/Si ratios are presented in Fig. 3 after heat treatment of the samples at 700 °C. The results illustrate that in the pure TiO_2 hollow spheres, rutile crystal phase is dominant in pure form without showing any crystalline peak such as anatase phase. But in the case of TiO_2 incorporated silica samples, the pattern shows that crystalline anatase phase (2θ=25.2°) is also present with the rutile phase. The (101) reflection of anatase phase gradually increases in the samples with greater TiO_2 loading. These results are in agreement with the results of Belhekar and coworkers [11] who prepared titania modified mesoporous silica by impregnation method.

UV-vis diffusion reflectance spectra of Ti/Si hollow spheres (calcined at 700 °C for 4 h) are shown in Fig. 4. The band gap of prepared samples could be determined by using the equation E_g=1239.8/λ [12]. The estimated band gap energies are about 2.83, 2.910, 2.889 and 2.889 eV for 0 wt%, 80 wt%, 70 wt% and 60 wt% Silica loaded titania-silica catalysts, respectively. The light absorption characteristics of the doped samples have not been affected with variation in

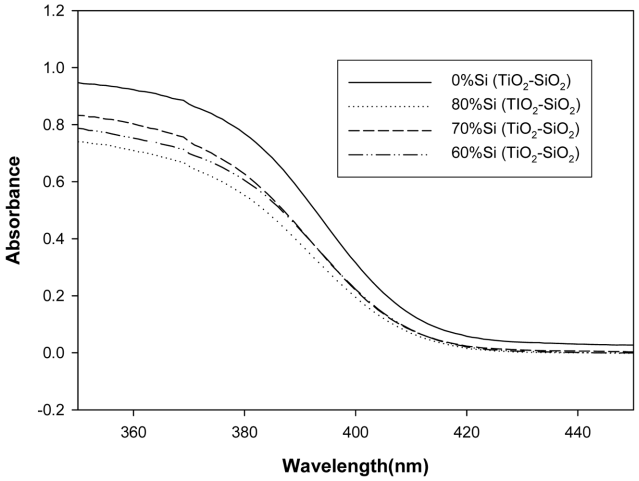


Fig. 4. DRS spectra of doped SiO_2 hollow spheres calcined at 700 °C with various Ti contents.

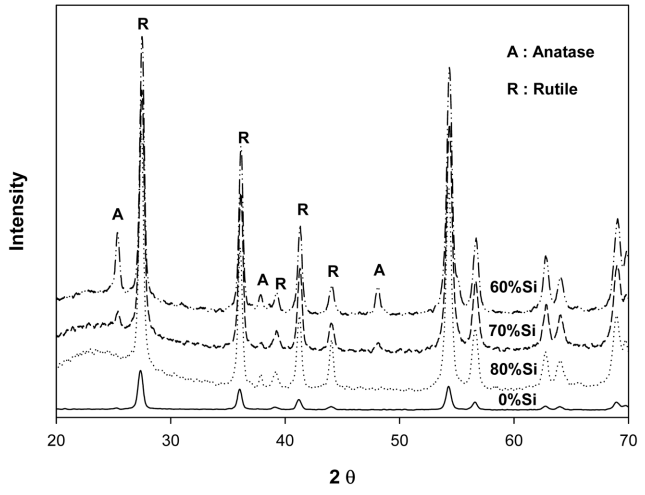


Fig. 3. XRD patterns of doped SiO_2 hollow spheres calcined at 700 °C with various Ti contents.

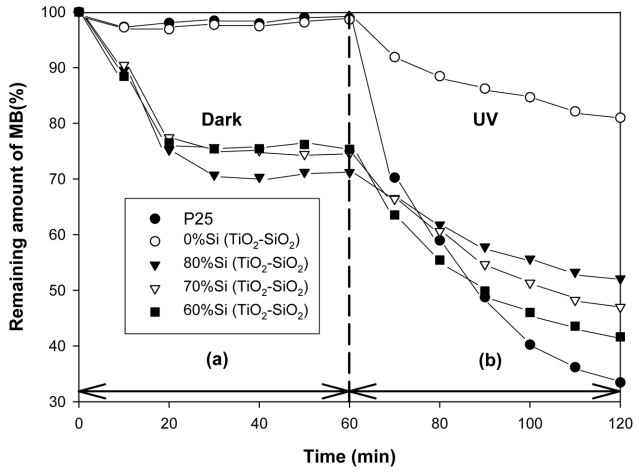


Fig. 5. Decomposition of MB by doped SiO_2 hollow spheres calcined at 700 °C with various Ti contents.

the TiO_2 loading. This increase in the band gap energy may be due to the inclusion of the anatase phase in the doped samples.

In Fig. 5, the photocatalytic degradation rate of MB has been shown by using calcined (700 °C for 4 h) TiO_2 doped SiO_2 hollow sphere samples of various compositions. In the figure, period (a) represents the initial duration of time (60 min for all the samples) for which the mixture of sample and dye solution was kept in dark condition with continuous stirring; whereas, period (b) denotes the result obtained after regular interval of 10 min, when the reaction mixture was exposed to UV irradiation. The results show that titania doped silica samples are more active in comparison to the pure TiO_2 hollow spheres during the adsorption of MB in dark. All the Ti/Si hollow sphere samples are good in adsorption of MB (period (b)). It may be related to the surface area of hollow sphere as shown in Table 1. Among the entire group of samples, 40 wt% TiO_2 doped SiO_2 catalyst has shown the best photocatalytic performance for the decomposition of MB. Although the photocatalytic activity of 40% TiO_2 doped SiO_2 hollow spheres is slight lower than that of P25, yet the adsorption of MB on the same sample was really remarkable.

CONCLUSIONS

SiO_2 hollow spheres were prepared by using poly-(styrene-methyl acrylic acid) latex particles as template. Prepared TiO_2 doped SiO_2 hollow spheres have a diameter value of 900-1,000 nm.

BET surface area value of Ti/Si samples has been diminished gradually with increase in the TiO_2 loading. The samples with highly dispersed TiO_2 nanoparticles on hollow SiO_2 have shown better photocatalytic activity. The photodegradation rate of MB using 40 wt% TiO_2 doped SiO_2 hollow sphere sample was 2.5 times greater than that by using pure TiO_2 in the same experimental conditions under UV irradiation. TiO_2 supported SiO_2 hollow spheres exhibited higher surface area and showed better photocatalytic activity than that of the pure TiO_2 hollow sphere sample.

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