

Preparation of Tin Oxide Doped Titania Catalyst and their Enhanced Photo Catalytic Activity under Solar Light Irradiation

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ABSTRACT

Tin oxide (0.5, 1 and 2 mol %) doped titanium dioxide catalysts are prepared by solution combustion synthesis method, using titanium isopropoxide, glycine and stannous chloride as the starting material. The prepared catalysts were characterized by X-ray diffraction (XRD), Energy dispersive X-ray analysis (EDX), Scanning electron microscopy (SEM) Infrared spectroscopy (FTIR) and BET Surface area measurement. Total acidity of the prepared catalysts were determined by temperature programmed desorption of ammonia (TPD-NH₃). XRD pattern of tin oxide doped titania obtained by calcinations at 873 K indicated that the samples were crystalline with a mixture of anatase and rutile phase. No peaks corresponding to tin oxide in the XRD patterns indicates that the amount of tin is negligible on the surface of titania catalyst. Methylene blue (MB) acts as an environmental pollutant in the dye industry. The photo catalytic activity was evaluated for the degradation of methylene blue under solar light irradiation. The enhancement of photo catalytic activity of titania by a second oxide, has been attributed to an increase in the surface area, change in the crystalline size, the predominant crystalline phase and modification in its band gap energy. Thus, this study synthesizes a visible light photocatalyst with a large surface area.

Keywords - Tin oxide doped titania, Solution combustion synthesis method, Environmental pollutant, Photo degradation of MB.

1. INTRODUCTION

The photocatalytic decomposition of dye pollutants in an aqueous solution using TiO₂-based photocatalysts has received a great of interest in recent years. The application of titanium dioxide as heterogeneous photocatalyst is attracting considerable attention for purification of air [1-3]. The attention has been recently focused on the semiconducting and photosensitive behavior, exploited in several applications concerning the environmental field, such as purification of air and water from pollutants [4] and solar cells for low-cost photovoltaic devices [5]. The major pollutants in textile effluent are dyes. Conventional treatment cannot remove dyes from textile wastewater effectively because they resist both light and biological degradation. The photocatalytic performance of TiO₂-based devices is largely influenced by the particle size, apparently at the nanometer scale.

Titania in anatase crystal form becomes the most promising photo catalyst for its efficient photocatalytic activity. However, its activity is hampered by some disadvantages such as relatively large band gap. Due to this large band gap (3.2 eV) of anatase form, all photon-

driven applications of TiO₂ require ultraviolet light for excitation [6]. Many attempts have been made to narrow the band gap energy by modification of TiO₂ using metal ions doping [7,8]. Incorporation of transition metal and rare earth ions were reported to improve the photocatalytic activity of TiO₂. These catalysts demonstrate significantly enhanced photocatalytic performance in the degradation of organic pollutants in air and water. They could facilitate charge transfer and suppress the recombination of electron-hole pairs in the photocatalysts.

Despite the promising properties, application is now limited for the UV region which occupies only near 4% of the entire solar spectrum. 45% of the solar energy belongs to visible light. More practical applications can be achieved if the photocatalytic active region can be expanded to the visible light region (400–700 nm); the photo energy can be used more efficiently [9]. As reported in the literature, Co and Fe doping [10,11] had increased the photocatalytic activity of TiO₂ under visible light. Nd³⁺ ion doping reduced the band gap of titania [12]. Xie et al. [13] reported that Sm³⁺ ions doping leads to considerable modification in the

photocatalytic activity of TiO₂ for cango red dye degradation under visible light.

To the best of our knowledge, few studies have been done using tin oxide. In our present study SnO is used as the dopand. Sn²⁺ can exist deeply in the lattice to alter the e⁻/h⁺ pair recombination rate through Sn²⁺/Sn⁴⁺ ions pair and give high charge carrier mobility. Synthesis of TiO₂ nano catalyst, were achieved by combustion method. The main advantage of the method is the reduction of the number of processing steps and the cost-effectiveness of the starting reactants. The study also aims at extending the light absorption spectrum towards the solar light region and to investigate the effect of the doping content of tin ions on the photocatalytic activity towards the degradation of methylene blue.

2. EXPERIMENTAL

The preparation of stannous oxide doped titania nano catalyst carried out by combustion synthesis method, using titanium isopropoxide (TTIP) and glycine as the starting material in 5:1 mol ratio. Desired amount of stannous chloride was used for the doping. Required amount of SnCl₂, glycine and a small amount of strontium nitrate were mixed together in finite form and to the above mixture TTIP is added drop wise and mixed well. Strontium nitrate was added to obtain ternary phases in the catalyst, which make tin oxide doped titania as a better catalyst. This is transferred to a silica crucible and combustion is done at 500⁰ C in a pre heated muffle furnace for 4 hours. 0.5, 1 and 2 mole % of tin oxide was used for doping on titania. The combusted puffy and porous powder obtained was sieved.

Powder X-ray diffraction (PXRD) measurements were performed on a PANalytical Xpert Pro X-ray diffractometer using Cu-K α radiation ($\lambda = 0.154$ nm) at 40 kV, at a scanning rate of 2^o min⁻¹. Energy dispersive X-ray analysis and SEM analysis was done in Quanta ESCM, FEI instrument. Fourier transform infrared (FTIR) spectra of the samples were recorded in a Bruker α -T instrument using the KBr pellet method. The BET surfaces of the catalysts were measured using nitrogen as an adsorbate at liquid nitrogen temperature in a Micromeritics Gemini surface area analyzer. Total acidity of the sample was determined by temperature programmed desorption of ammonia.

The photo catalytic activity of the prepared catalysts was evaluated by photo degradation of methylene blue dye at desired concentration (2.8×10^{-5} M) under solar

light irradiation. This photo catalytic activity was performed between 10 am to 3 pm during the summer season in Bengaluru, India. The latitude 12.58 N and longitude 77.3 E. The average intensity of sunlight was around 1350 Wcm⁻². The catalyst (0.02g) was suspended in methylene blue (MB) aqueous solution and was irradiated with solar light for different time intervals. The decolourization of MB was recorded and calculated before and after the reaction using a Shimadzu UV-Vis 1800 Spectrophotometer from 400 to 800 nm.

3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the prepared samples. Titania shows both anatase and rutile phases after calcination at 500⁰ C. X-ray diffraction peak at 25.5^oC corresponds to (101) plane of anatase and the peak at 27.6 ^oC corresponds to (110) plane of rutile [13]. No characteristic peaks corresponding to SnO₂ ($2\theta = 25.12^{\circ}$) were observed in the tin doped titania, which implies complete doping of tin ions in the lattice of TiO₂.

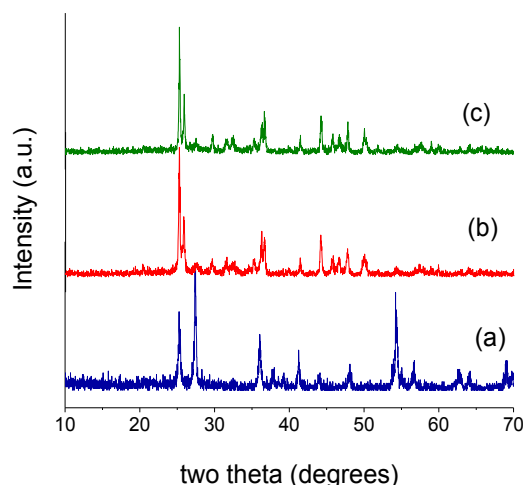


Fig. 1 PXRD patterns of (a) TiO₂ (b) 0.5SnTiO₂ and (c) 2SnTiO₂

The relative intensity of (101) of anatase phase and (110) of rutile phase were calculated (Table 1) using the equation $X_R = (1 + 0.8I_A/I_R)^{-1}$ [14]. The crystallite sizes of the samples were calculated (Table 1) using Scherrer equation: $d = 0.9\lambda/\beta\cos\theta$ Here, d represents the crystalline size (nm); λ is the wavelength of the X-rays (0.15418 nm); β is the line-width at the half maximum of the anatase peak at $2\theta = 25.4^{\circ}$ or of the rutile peak at $2\theta = 27.5^{\circ}$, and θ is the diffraction angle. The crystallite size of the anatase and rutile phase of the prepared catalysts varies from 8-13 nm. As the mol % of tin

oxide increases, the intensity of anatase and rutile phase decreases.

Table 1: Surface parameters of the catalysts

Mole % of tin oxide	Crystallite size (nm)		Relative intensity		BET surface area (m ² /g)
	Anatase d ₍₁₀₁₎	Rutile d ₍₁₁₀₎	X _A %	X _R %	
0	12	11		85	58
0.5	7	7		85	121
1	9	8		78	98
2	10.4	11		82	85

Table 1 shows the surface parameters of the prepared catalysts. Surface area of the tin doped titania is higher than that of undoped titania. The reduction in specific surface area was attributed to the formation of agglomerates at higher tin loadings, as indicated by SEM studies. As the surface area reduces, the active sites on catalyst available for the adsorption of reactants also reduce. Pawar and co-workers had reported that, calcination temperature > 600°C is not helpful for the photocatalytic activity of the doped TiO₂ nanoparticles [15]. The SEM images (Fig. 2) of the samples showed homogeneous and crystallized particles with size ranging from 80-100 nm.

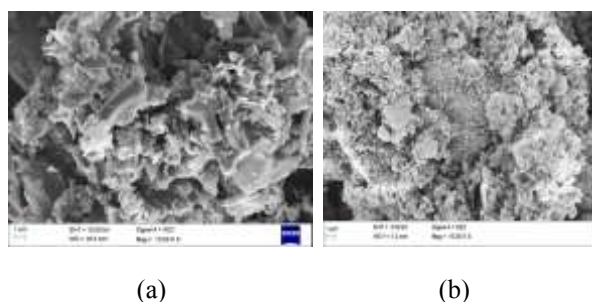


Fig. 2 (a) SEM images of (a) TiO₂ (b) 2SnTiO₂

From EDX data it is concluded that the weight composition of Ti is 60.8% and O is 39.2% in TiO₂. In the case of 2 mole % tin doped oxide titania, the weight composition of Ti, O and Sn in the samples were calculated and is in the order 9.8%, 28.7% and 2.2% respectively. In 2 mol % Tin oxide doped titania the particles are become spherical in shape and the size of the particles varies in the range of 8.9 – 11.5nm. The introduction of Sn⁴⁺ ion decreases the size of the particle and spherical shape [16].

The FTIR spectrums of the synthesized catalysts were obtained in the range of 400- 4000 cm⁻¹. The spectrum of TiO₂ (Fig. 3) before calcinations shows the bands between 3500 and 3150 cm⁻¹ which corresponds the H-bounded hydroxyl groups. These bands disappear after heating. The bending vibration mode of O-H of water molecule after calcinations is observed at around 1456 cm⁻¹ [17]. In 2SnTiO₂ (Fig. 3) the absorption band around 3450 cm⁻¹ is due to physically adsorbed water molecules. Ti–O–Ti stretching frequencies of tin doped titania was seen around 613 cm⁻¹. No separate peaks corresponding to tin oxide were seen which indicates complete doping of tin in titanium dioxide [18].

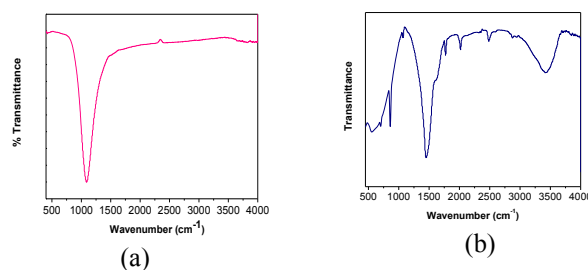


Fig. 3 FTIR spectra of (a) TiO₂ (b) 2SnTiO₂

The TPD of ammonia was used to characterize the acid site distribution and furthermore to obtain the quantitative amounts of acid sites in the specified temperature range. The distribution pattern can be classified into weak (desorption at 100-200⁰ C), medium (200-400⁰ C) and strong (400-600⁰ C) acid sites. Among the modified samples 2SnTiO₂ shows maximum acidity. Acidity increases slowly from 0.5 to 2 mole% loading of tin oxide (Fig. 4). The natures of the acid sites are greatly altered by the nature of the ions incorporated into the lattice. The distribution change may be a coupled effect of the structural and crystalline changes. It has been already reported that the change in the acid strength distribution for the doped catalysts can be because of the interaction of the added metal oxides with TiO₂ [19]. With increasing concentration of dopants, the amount of reactive acid sites available for the adsorption of catalyst also increases.

The photo catalytic activity study of TiO₂ and tin oxide doped TiO₂ was carried out in the presence of MB cationic dye. It is known as a photo fading catalyst and act as an environmental pollutant. It is used in textile manufacturers for dyeing cotton, wood and silk. It releases aromatic amines like benzidine, methylene etc, which is a potential carcinogen. These synthetic dyes released from industries deposited in the nearby water

bodies and pose threat to the aquatic life as they are non-degradable in nature.

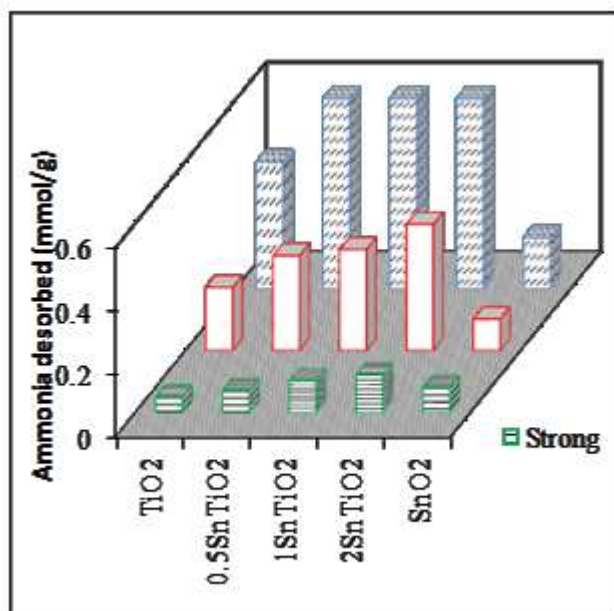
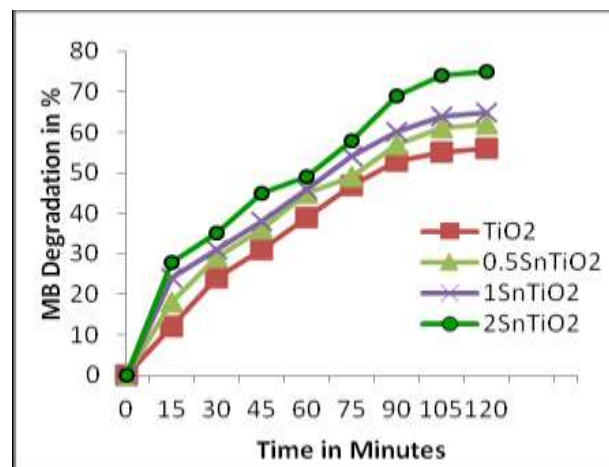


Fig. 4 Acid site distributions as obtained from NH₃-TPD studies

Photo degradation study of MB dye was carried out under diffused sunlight with different reaction parameters and optimized as follows. Concentration of MB as 2.8×10^{-5} M, amount of the catalyst as 0.02g and time of solar irradiation as 2 h. At regular intervals, the decolorization of MB was visually observed and the rate of colour change was studied by recording the UV-Visible spectrum. There is a prompt removal of the colour of MB after solar light irradiation in presence of the prepared catalyst. This is due to more MB ions adsorbed on the surface of TiO₂ and reacted with the free radicals. This can also be due to the self-photo fading property of the MB catalyst. From the studies (Fig. 5), 2 mol% of tin oxide is an optimal concentration for photo catalytic activity of TiO₂. 2SnTiO₂ exhibited high photo catalytic activity which suggests that, due to more doping of the ions behave as an electron-hole trapping centre. Similar results having already been reported for Nd³⁺ and Er³⁺ on titania [20,21]. Thus all the doped TiO₂ compounds enhance the photo catalytic activity of TiO₂ and there is an optimum doping content of ions on titania surface.

Chakraborty and coworkers had reported the importance of Lewis acidity in photo catalytic activity under visible light irradiation [22]. Strong acid sites are more in 2SnTiO₂, which could be favored the reaction. The larger surface area of doped TiO₂ catalysts would

be beneficial to achieve better adsorption of MB in aqueous suspension. Therefore, the increase of doped ion content seems to be helpful for the photo catalytic activity. However, doping beyond the optimal percentage would hamper the photo catalytic activity of the catalyst due to lowering separation efficiency of electron-hole pairs. Xu *et.al* reported that there exists an optimum doping content of rare earth ions in TiO₂ particles for the most efficient separation of photo induced electron-hole pairs [23].



Amount of catalyst: 0.02g, Conc. of MB: 2.8×10^{-5} M

Fig.5 Effect of Mol % on MB Degradation of tin oxide doped titania

4. CONCLUSION

Solution combustion synthesis method is a promising technique for the preparation of TiO₂ and SnO doped TiO₂. XRD studies reveal the presence of anatase and rutile phase in the catalysts. Tin oxide was well dispersed on the titania surface. Acidity and surface area are higher for tin topped titania. The surface acidity of the catalysts was maximized at 2SnTiO₂. Strong acid sites are more for 2SnTiO₂ compared to other synthesized samples. A strong electron-hole trapping centre can create strong adsorption behavior towards the organic compounds compared to TiO₂. MB act as an environmental pollutant and it cause a threat to aquatic life. These prepared catalysts can be used to remove the MB from the water bodies in presence of renewable source of solar energy. These are highly efficient photocatalysts, may have potential applications in the removal of other pollutants from air and water.

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