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Surfactant mediated synthesis of spherical binary oxides photocatalytic with enhanced activity in visible light

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ABSTRACT

Spherical silica and zirconia mixed titania and pure titania samples were prepared in presence of cetyltrimethylammonium bromide (CTAB) through controlled hydrolysis of corresponding metal alcoxides. Effect of surfactant amount and calcinations temperature on morphology, surface area and photocatalytic activity is studied using PXRD, SEM, FTIR, Solid state UV–vis spectroscopy and BET surface area. It is well observed that in presence of 2 mol% CTAB, uniform sized spherical oxide particles can be synthesized. However, increasing or decreasing the surfactant amount does not favor the spherical particle formation. Material synthesis in presence of CTAB not only helps in the spherical particle formation but also increases the surface area and visible light absorption. Studies on photocatalytic lead removal with respect to calcination temperature indicate that the calcination at 500 °C is most suitable for the best photocatalytic activity. Mixing of zirconia and silica helps in anatase phase stabilization even at 900 °C calcination. Accordingly low decrease in surface area even at 900 °C calcination is observed. Due to the phase stabilization and higher surface area binary oxide materials showed comparatively better photocatalytic activity even after calcination at 900 °C. So it can be concluded that present synthesis approach can produce uniform sized spherical binary oxide materials with better photocatalytic activity in visible light.

1. Introduction

Synthesis and performance analysis of photocatalytic materials continue to be the areas of great research interest for the decontamination of different water sources. In this context titanium dioxide is most widely studied as photocatalytic material with various modifications during the synthesis process due to its nontoxic and chemically stable nature [1,2]. However, the effectiveness of the performance of a photocatalyst depends on a number of factors such as the crystal structure [3,4], surface functionality [5,6] and the surface accessibility [1,2] of the catalyst. Methods used to control these characteristic include doping of titania or the addition of another metal oxide to the titania thereby regulating the phase transitions of the crystal and changing the surface properties by the formation of composite materials. In this context it was also observed that doping with transition metals increases the visible light absorption [7]. The incorporation of transition metal into the anatase phase of TiO_2 has been frequently studied as a way to extend the spectral response to the visible range [8]. In addition, certain $Ti_{1-x}M_xO_2$ phases show an enhancement of the photoactivity due to structural and electronic modifications induced by the dopant. In this respect, the inclusion of Sn^{4+} in the rutile and the anatase structures leads to a significant increment of the rate of photocatalytic oxidation of acetone [9] or methylcyclohexane vapor. Whereas doping with lanthanides facilitates visible light absorption by decreasing the band gap for visible light absorption [10]. In the recent years many mixed oxide systems were reported as potential photocatalyst due to the different nature of the binary oxide systems over pure titania [11,12]. WO_3 coupling has been widely used to improve the photoelectrochemical and photocatalytic performance of TiO_2 since WO_3 is more acidic than TiO_2 and can serve as an electron accepting species [13,14]. In particular addition of ZrO_2 was found to be beneficial as it inhibited the anatase to rutile phase transformation [15,16]. Similarly mixing of silica also increases the catalytic activity particularly in presence of UV light. Anderson and Bard [17,18] reported that a mixed oxide powder of TiO_2 and SiO_2 can be more efficient photocatalyst than pure TiO_2 powder. On the other hand nonmetal doping of TiO_2 rekindled a great interest in visible light catalysis since the report of the work of Asahi et al. [19]. It is observed that doping with nonmetals like N [19], C [20], F [21], etc. can increase the visible light

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absorption of the photocatalyst. There are several reported methods for nonmetal doping on the semiconductor oxide materials. One of the studied methods is of mixing nonmetal containing compounds with titania through milling followed by calcinations [22, 23]. Generally calcinations of the said material at high temperature ($>500\,^{\circ}\mathrm{C}$) is required to achieve effective doping in the crystal lattices of photocatalyst. However, the required heat treatment often leads to a loss of surface area which ultimately reduces the light harvesting capability and catalytic activity of the material. Simplest process is the sol–gel synthesis in presence of a nonmetal containing compound which can results in nonmetal doped products even at low pretreatment temperature [24–26]. In particular surfactant mediated synthesis of mesoporous photocatalysts with improved activity are reported [27–30] in the literature. In our earlier report we have also demonstrated the improved photocatalytic activity of binary oxide prepared in presence of surfactant [31]. In continuation of our reported work here we have tried to investigate the role of surfactant concentration and calcination temperature on the physico-chemical properties and photocatalytic lead removal activity of the prepared materials. Moreover the said materials are found to be effective photocatalyst even in visible light mostly due to the N doping of synthesized material.

2. Materials and methods

2.1. Material synthesis

Titanium isopropoxide, zirconium butoxide and tetraethyl orthosilicate (Aldrich) were used as starting material. Materials were synthesized according to the earlier reported method [31] by only varying the surfactant concentration. Pure titania and silica, zirconia mixed titania were prepared by controlled hydrolysis of corresponding isopropoxide in presence of surfactant (cetyltrimethylammonium bromide, CTAB) in *n*-propanol water mixture. Silica and zirconia (10 and 20 wt%) mixed titania samples were prepared by using calculated amount of corresponding alcoxide mixture in *n*-propanol so as to maintain the ratio of 10:90 and 20:80 in the binary oxides. Surfactant concentration was varied from 0 to 4 mol% and accordingly required amount was added to the reacting mixture before hydrolysis. Hydrolysis was carried out by drop wise addition of *n*-propanol and water mixture from a burette under magnetic stirring condition in 30 min time period. The gel so obtained was maintained in the same stirring condition for another 4 h. Subsequently the gel was filtered and washed with distilled water several times, dried at 100 °C, calcined at 500, 700 and 900 °C for 4 h and kept for further use. Silica mixed titania and zirconia mixed titania are denoted as TiSi and TiZr, respectively. Number after the sample indicates the weight percentage of silica or zirconia mixed with titania.

2.2. Material characterization

XRD patterns of all the synthesized samples calcined at different temperatures were recorded on a Siemens (model: D-500) semiautomatic diffractometer using CuK_α radiation source and Ni filter in the range of 10° to 70°.

BET surface area was determined by N_2 adsorption desorption method at liquid nitrogen temperature using Quantasorb (Quantachrome, USA). Prior to adsorption desorption measurements, the samples were degassed at 393 K at 10^{-4} Torr for 5 h.

SEM micrographs of powdered samples were recorded on scanning electron microscope (JEOL 840A, Japan) after gold coating.

FT-IR spectra of different samples were recorded with Nicolet 750 FT-IR spectrometer using KBr palate at room temperature in the range of 400 to 4000 cm^{-1} with scanning rate of 4 cm^{-1}/min.

2.3. Photocatalytic activity

Prepared materials after calcination at different temperatures were used as photocatalyst for the reductive removal of lead metal ions in acidic pH. Stock solution of lead was prepared by dissolving required amount of corresponding nitrate salts in double distilled water. All the photocatalytic experiments were carried out in a 200 ml capacity three necked glass reactor fitted with 125 w visible lamp under magnetic stirring condition. Constant reaction temperature was maintained through water circulation in the outer jacket of the glass reactor. All the experiments were performed in presence of air at atmospheric pressure. Initial concentration of metal ions was maintained at 100 ppm in each experiment. Sodium formate (200 ppm) is used as the hole scavenger for all the experiment. After the reaction, metal deposited solid catalyst was separated by centrifuge. Metal ion concentration in the solution after and before reaction was estimated by AAS.

3. Result and discussion

In the initial experiments we varied the surfactant content from 0 to 4 mol% during titania synthesis to see the effect of surfactant concentration on the particle shape and size. Interestingly, we observed the formation of uniform sized spherical particles (Fig. 1) only with 2 mol% of CTAB. So other materials like silica and zirconia mixed titania were synthesized keeping the CTAB concentration at 2 mol%. Again we found the formation of spherical particles for all the binary oxide samples. So it seems that the surfactant concentration plays an important role in deciding the sphericity of the material irrespective of the presence of other oxides up to 20 wt%.

3.1. Textural characterization by XRD

All the materials are found to be amorphous in nature after calcination at 400 °C. However, materials calcined at 500 °C shows low crystallinity of anatase phase as evident from Fig. 2. The crystallinity of the materials increases with the increasing calcination temperature. It is observed that pure titania completely transformed to rutile phase even at 700 °C calcination. However, the other four binary oxide materials show the presence of clear anatase phase after calcination at 700 and 900 °C (Fig. 3). This justifies the phase stabilization effect of silica and zirconia even at low concentrations. Moreover with 10 wt% silica and zirconia samples, no extra phase formation is observed at all calcinations temperature. A new zirconium titanate phase (TZ) is observed (Fig. 3) particularly at 900 °C calcination in case of 20 wt% zirconia sample only. Broad peak of 101 reflection (Fig. 2) conforms the nanocrystalline nature of the anatase phase. However, with the increase in the calcination temperature the peak became sharper indicating the increase in the crystallite size. Peak sharpening is clearly marked incase of pure titania with the increase in calcination temperature. Crystallite size calculated from the XRD line broadening technique is tabulated in Table 1 which also supports our argument. The anatase peak remains broad with low crystallite size even at 900 °C calcination for most of the binary oxides. This effect is more pronounced for the silica mixed samples. In case of zirconia mixed samples, peak is sharper with the increase in the zirconia content. Accordingly crystallite size also increases.

3.2. Particle shape, size and porosity

SEM micrographs of all the materials calcined at 500 °C temperature were presented in Fig. 4. At 500 °C calcination all the materials maintain spherical shape with average particle diameter within 800–1200 nm. Particle size distribution calculated using Erfan view