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Photocatalytic degradation of dye pollutant over Ti and Co doped SBA-15: Comparison of activities under visible light

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ABSTRACT

Thick-walled hexagonally ordered Cobalt and titanium loaded SBA-15 mesoporous photocatalysts were prepared by impregnating the metal precursor solution on the hydrothermally stable support. The catalysts were analyzed using various spectroscopic and diffraction techniques. XRD measurements revealed that Co exists as its spinel structure Co_3O_4 and Ti is present in the anatase TiO_2 phase. FTIR showed the absorption bands of Co_3O_4 around 667 and 565 cm^{-1}. The visible light absorbance of the photocatalytic systems was studied by Diffuse Reflectance Ultraviolet–Visible spectroscopy (UV–vis DRS) measurements. Systems exhibited fairly good performance as photocatalysts for pollutant degradation under visible light. SBA-15 support was helpful in the easy separation of catalysts after the completion of the degradation. In the case of cobalt loaded SBA-15, activity is found to be maximum when the cobalt loading is 40% whereas 50% Ti loaded SBA-15 is found to be the most active among the prepared systems for the degradation of the dye pollutant methylene blue (MB).

1. Introduction

Photocatalysis is a widely used technique for the abatement of environmental pollutants and have attracted considerable attention in recent past. The superiority of photocatalytic technique in wastewater treatment can be attributed to its advantages over the traditional techniques, such as quick oxidation, no formation of polycyclic products, oxidation of pollutants in the ppb range, etc. The use of semiconductor heterogeneous photocatalysts for the degradation of organic pollutants is an area where a lot of research work is going on. Many semiconductor oxides like TiO_2, Fe_2O_3, ZnO, ZrO_2, Nb_2O_5, WO_3, Bi_2O_3, SnO_2, etc. have been employed as photocatalysts in the wastewater treatment [1–3]. TiO_2 is the most investigated semiconductor photocatalyst in the past decade [4]. However, the major limitation of this technique is the poor visible light harvesting since the absorption wavelength of anatase does not conform to the visible light region of solar spectrum [5]. Many modification methods are available to shift the absorption of TiO_2 to the visible region and now other transition metal ions are also effective in the field of pollution abatement [6]. Among transition metal oxides, Cobalt oxides are reported to show good photoactivity for pollutant degradation [7–9].

One difficulty arising in the usage of nano TiO_2 and CO_3O_4 based catalytic systems is the separation of catalyst in the end. The filtration problems have been eliminated to a large extent by the development of supported photocatalysts in which metal oxides are immobilized on different adsorbent materials. In this context, molecular sieves have attracted greater attention due to their adsorption capacity that helps in pooling the pollutants to the vicinity of the metal oxide surface resulting in faster degradation [10–12].

Mesoporous materials are widely used as catalysts and hosts for nanomaterials synthesis because of their highly ordered and uniform mesoporous channels and large surface area (usually more than 800 m^2/g). Uniform ordered channels of mesoporous materials can control the particle size of TiO_2 and Co_3O_4 and can efficiently prevent particles from agglomeration [13]. Pure silica is having no active sites in their matrices. Active sites can be generated via chemical modification, i.e. by the introduction of heteroatoms into the silica matrix [14,15], and activity can be improved further. There are several reports in the literature about photocatalysis using transition metal incorporated mesoporous silicates such as Al, Ti, Cr, Fe, and Mn [16,17]. When 2,9-dichloroquinacridone sensitized Ti-SBA-15 (DCQ-Ti-SBA-15) was employed to decompose indigo carmine, high photocatalytic efficiency was shown, under UV light irradiation [18]. The photocatalytic performance of the

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titania–silica mixed oxides (mass ratio of Ti/Si = 0.5) with crystalline titania for the degradation of methyl orange dye under UV light has been reported by Li et al. [19]. Photocatalytic degradation of methylene blue (MB) had been reported over Ti and Co doped SBA-15 catalysts [20–24]. Most of the studies used UV light for irradiation. Xia et al. [25] had tested the activity of Co/SBA-15 under sunlight. There the samples are found to be amorphous in nature and no peaks of Co_3O_4 spinel, the most photoactive form of cobalt oxide is observed.

In the present study, efficient dispersion of Co_3O_4 spinel and TiO_2 is done on SBA-15 by impregnation method and the properties are analyzed using XRD, FTIR, FESEM, BET surface area – porevolume measurements and UV–vis DRS experiments. Activity for pollutant degradation is tested under visible light. Influence of the percentage metal loading on the properties and photodegradation activity is investigated. The SBA-15 support material is prepared using hydrothermal method. The visible light photoactivity is monitored by the degradation of a model aquatic pollutant methyleneblue (MB).

2. Experimental

2.1. Preparation of SBA-15

The support, SBA-15 material was prepared using the method already reported [26]. In a typical synthesis 4.4 g Pluronic P123 (Aldrich, $M_{avgerage}$ = 5800 [EO20-PO70-EO20]), 120 g of 2 M HCl (R&M chemicals) and 9 g TEOS (Aldrich) were required. Typically 4.4 g of triblock copolymer was dispersed in 30 g-distilled water and stirred for 1.5 h. To the resultant solution, 120 g of 2 M HCl was added under stirring and the stirring was continued for 2 h. Finally, 9 g of TEOS was added drop wise and the mixture was maintained at 35 °C for 24 h without stirring. The resulted heterogeneous mixture was subjected to hydrothermal treatment at 100 °C for 48 h under static condition before recovering the solid material. The crystallized product was filtered, washed with distilled water and dried in air for 24 h and in oven at 70 °C for overnight, and then calcined at 450 °C for 8 h in air to remove the template completely.

2.2. Preparation of cobalt and titania loaded SBA-15

Cobalt and Titania loading was done on SBA-15 by simple impregnation method. The cobalt nitrate hexahydrate (Hamburg Chemical GmbH) was dissolved in ethanol. A predetermined amount of prepared SBA-15 was then added to this solution, followed by heating at 60 °C for removal of the solvent. The amount of cobalt nitrate is varied to get different wt% of cobalt/g SBA in each impregnation. The concentrated sample was then dried in oven at 55 °C for overnight. The dried sample was then calcined at 450 °C for 3 h. The same procedure was repeated with Titanium isopropoxide (Aldrich) to get Titania loaded SBA-15 and the catalysts are designated as 40Co/SBA, 50Co/SBA, 40Ti/SBA, 50Ti/SBA where the numbers indicates the percentage metal loading.

2.3. Catalyst characterization

XRD patterns of the samples were recorded for 2θ between 10° and 80° on a Bruker AXS D8 Advance diffractometer employing a scanning rate of 0.02°/S with Cu Kα radiation (λ = 1.5418).

Low angle XRD patterns of the samples were recorded for 2θ between 0.5° and 10° on a Bruker D8 Advance diffractometer with Cu Kα radiation (λ = 1.5418). The formation of well ordered mesopores of SBA-15 is confirmed from TEM images (ZEISS LIBRA 200). The FTIR spectra were recorded in NICOLET 6700 FT-IR Thermoscientific spectrometer in the region 400–4000 cm^{-1}. BET surface area and pore volume were measured by TriStar 3000 V6.04 A, using nitrogen physisorption at −195.800 °C. The specific surface area was estimated by the BET method. The pore size distribution and pore volume was determined by the BJH method. The morphology studies were carried out using a Field Emission Scanning Electron Microscope SU6600 (HI-2102-0003). Diffuse Reflectance Ultraviolet–Visible spectroscopy (UV–vis DRS) of powder catalyst samples was carried out at room temperature using a Varian, Cary spectrophotometer in the range of 200–800 nm.

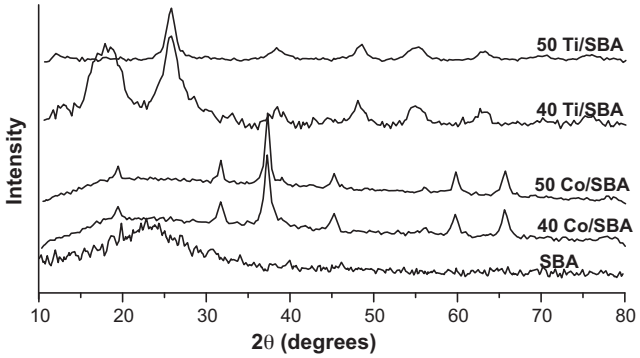

Fig. 1. XRD patterns of the prepared systems.

2.4. Photocatalytic degradation

Photocatalytic activity of the prepared materials was evaluated for degradation of methylene blue as a model compound. The pollutant degrading capacities of the different systems were studied using a Rayonet type Photoreactor with visible light having 16 tubes of 8 W (Associate Technica, India). In the reactor, 5 glass tubes were concentrically arranged to get uniform illumination for all the systems. 50 mL of MB was placed in the glass tube, containing a definite amount of the catalyst and is irradiated with visible light under continuous stirring. In a typical experiment, the required amount of catalyst were suspended in 50 mL of the MB solution and kept for overnight in the dark to reach to the maximum adsorption equilibrium. The MB concentration was analyzed using a colorimeter (ESICO Microprocessor photo colorimeter model 1312) at a wavelength of 665 nm. For optimization studies, the catalyst weight, dye concentration, irradiation time, etc. are varied to compare the efficiency of catalysts.

3. Results and discussion

3.1. Structural characterization

The photocatalytic activity of semiconductors depends on various parameters, such as crystallinity, impurities, surface area, and density of surface hydroxy groups. However, the most significant factor is their crystal forms. TiO_2 is usually used as a photocatalyst in two crystal structures: rutile and anatase. Anatase generally has much higher activity than rutile. Fig. 1 represents X-ray diffraction patterns of the calcined SBA-15 and metal loaded samples. From the figure it is clear that titania is in most active anatase form. The strong peak at 2θ = 25.41, belongs to anatase phase. In the case of Co/SBA samples the peak around 2θ value 36.8° indicates the formation of spinel cobalt oxide, Co_3O_4. Both the Co/SBA catalysts showed peaks at 2θ values of 31.48, 37.18, 59.38, and 65.28, which can be attributed to the presence of crystalline Co_3O_4 (JCPDS 42-1467) [27]. Co_3O_4 is reported to show greater photoactivity when compared to other cobalt oxides. The crystallite sizes calculated using Scherrer equation is tabulated in Table 1. TiO_2 containing samples are found to show least crystallite size when compared to Co_3O_4 crystallites and it is seen that the crystallite size increases