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Enhanced adsorptive and photocatalytic achievements in removal of methylene blue by incorporating tungstophosphoric acid–TiO_2 into MCM-41

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ABSTRACT

The use of titania-dispersed materials in photocatalytic processes has been proposed as an alternative to the conventional bare TiO_2, in order to modify the surface area and activity of the catalyst. A homogeneously dispersed Keggin unit into TiO_2 was synthesized using tungstophosphoric acid (TPA) and titanium tetraisopropoxide. This compound was then loaded into MCM-41 by dispersing it in a suspension containing the mesoporous phase. Two other titanium-containing MCM-41 catalysts, Ti–MCM-41 and TiO_2/MCM-41 were also prepared using isomorphous substitution synthesis method and impregnation method, respectively, for the sake of comparison. The prepared photocatalysts were characterized by X-ray diffraction (XRD), nitrogen physisorption (BET) and chemical analysis. The catalysts were used to study degradation of methylene blue (MB) in aqueous solution. XRD result shows a pure anatase crystalline phase for TPA-containing TiO_2 indicating that there is good molecular distribution of tungstophosphoric acid into TiO_2 structure. Supported TPA–TiO_2 into MCM-41 shows both TPA–TiO_2 and MCM-41 characteristic X-ray reflections in the high-angle and low-angle parts of the XRD patterns, respectively. The experimental results show that adsorption is a major constituent in the elimination of MB from the dye solutions by the TPA-containing materials. Exploitation of both adsorption and photocatalytic processes speeds up the removal of the dye using the TPA–TiO_2-loaded MCM-41 photocatalyst. The elimination of MB is completed within 15 min for a 30 mg l^{-1} MB solution containing a catalyst dose of 100 mg/100 ml. The efficiencies of the other photocatalysts such as commercial TiO_2, Ti–MCM-41, TiO_2/MCM-41 and TPA–TiO_2 for adsorption and degradation of MB were also studied and compared with that of the prepared catalyst.

1. Introduction

In recent years, there has been a magnificent amount of research and development in the area of photocatalytic degradation and heterogeneous photocatalysis. Heterogeneous photocatalysis is an attractive and highly efficient method for degradation of toxic and non-biodegradable environmental pollutants commonly present in domestic or industrial wastewater [1–9]. These processes are based on the use of UV radiation to excite a semiconductor material, usually TiO_2, which on its surface the oxidation of the pollutants is performed. TiO_2 is chemically and biologically inert, photocatalytically stable, commercially available and inexpensive, and environmentally friendly [2,10]. However, there are certain limitations of using bare TiO_2 in photocatalyst reactors. To have an adequate TiO_2 photocatalytic activity, particles should be small enough to offer a high specific surface area. But due to this small size (about 30 nm) TiO_2 aggregates rapidly in a suspension loosing its effective surface area as well as the catalytic efficiency. In addition to that, application of such small particles imposes a high filtration costs to remove the catalyst when the reaction is finished. These problems have prompted the development of supported photocatalysts in those TiO_2 has been immobilized on the porous adsorbent materials. Some of the recent studies have reported the use of silica [11–13], clay [14], polymer film [15], activated carbon [16–18], and zeolites [19,20] as an effort to increase the efficiency and performance of the catalysts.

In the last decade, supporting TiO_2 on the mesoporous materials [19–26] has attracted considerable attention because of their very large surface area, controllable pore size and narrow pore size distribution. They are usually loaded with TiO_2 by sol–gel [21–24] or impregnation [19,20,25] methods. One of the most interesting mesoporous materials is MCM-41 which is an inorganic silica based material and exhibits a uniform hexagonal arrangement of cylindrical pores. Although, numerous works have been reported on the immobilization of TiO_2 on MCM-41 materials, detailed characterization and performance evaluation in different applications are lacking.

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Another approach to increase surface area of TiO_2 and therefore to improve its catalytic activity is to make mesoporous TiO_2. This is achieved by using suitable pore-forming agents including surfactants [27,28] or organic compounds [29,30]. However, synthesizing mesoporous TiO_2 is not as simple as that of mesoporous silica due to higher reactivity of the former towards hydrolysis and condensation [31]. If this reactivity is not controlled, the synthesis will lead to an ill-defined and poorly ordered structure. Therefore, there are methods and challenges to synthesize stable mesoporous TiO_2 with a high surface area and suitable ordered form [32–35]. Recently, Huang et al. reported synthesis of mesoporous TiO_2 particles using tungstophosphoric acid at the absence of any template [36]. The material lacks long-range ordering of pores because of the absence of template that controls the packing of micellar rods. Yang et al. have also reported synthesis of TiO_2 photocatalyst containing homogeneously dispersed tungstophosphoric acid by combined sol–gel and programmed temperature hydrothermal method [37]. Their composite materials show photocatalytic activity for decomposition of various organic dyes. They suggested that the higher photocatalytic activity of tungstophosphoric acid–TiO_2 compared to traditional TiO_2 is mainly originated from the synergistic effect produced by the combination of polyoxotungstate unit ($H_3PW_{12}O_{40}$) and TiO_2. According to this consequence, the interfacial electron transfer takes place from the TiO_2 conduction to $H_3PW_{12}O_{40}$ after irradiation. Such an effective electron transfer can inhibit the fast electron–hole recombination on TiO_2.

In this contribution, we tried to improve the activity of $H_3PW_{12}O_{40}$–TiO_2 composite (TPA–TiO_2) by supporting it onto MCM-41 (a mesoporous material) to combine the synergestic effect of the former with the high stability and large surface area of the later. Modification of the surface of MCM-41 by introduction of bulky group of TPA–TiO_2 to its structure produced an efficient adsorbent and photocatalyst based on TiO_2. This catalyst is used for photodegradation and mineralization of methylene blue. Methylene blue is a pollutant dye chosen as the model compound to determine the photocatalytic activity of the supported TiO_2 in aqueous medium. The performance of the supported TiO_2 in degradation of the dye is studied under different operating conditions and the results are compared with that of commercially available TiO_2^-.

2. Experimental

2.1. Reagents and materials

The commercially available TiO_2 powder was in anatase crystalline form with purity of 99% purchased from Merck. Tetraethyl orthosilicate (TEOS) was purchased from ACROS. N-cetyl-N,N,N-trimethyl ammonium bromide (CTMABr), tungstophosphoric acid ($H_3PW_{12}O_{40}$: TPA), ethylamine, ethanol, methylene blue, HCl, isopropanol and tetraisopropyl orthotitanate (titanium tetraisopropoxide) were obtained from Merck.

2.2. Preparation of photocatalyst

The TPA–TiO_2 composite was prepared with little modification in the described procedure in the literature [37]. In a typical experiment, 6 ml titanium tetraisopropoxide (TTIP, 98%) was dissolved in 30 ml of isopropyl alcohol while stirring was used. In another container, 0.4 g of $H_3PW_{12}O_{40}$ (TPA) was dissolved in 0.8 ml of water and then it was added into the TTIP solution drop by drop. The resulting mixture was adjusted to pH 1–2 by the addition of 8 mol l^{-1} HCl, and then stirred at room temperature for 1 h. The mixture was heated to 45 °C until homogeneous hydrogel was formed. This hydrogel was transferred into an autoclave, and then heated to 200 °C at a heating rate of about 2 °C min^{-1}. Finally the temperature was kept at 200 °C for 1 h. After cooling the TPA–TiO_2 hydrogel to room temperature, it was dehydrated slowly at 50 °C for 24 h. The dried gel was washed with hot water three times, and then dried at room temperature. The product is white powder.

The parent purely siliceous MCM-41 was synthesized by a room-temperature synthesis method as described previously [38]. We used TEOS as a source of silicon and CTMABr as template for preparation of MCM-41. The procedure for MCM-41 synthesis is as follows: 2.7 g ethylamine was added to 42 ml of deionized water and the mixture was stirred at room temperature for 10 min. The amount, 1.47 g of surfactant (CTMABr) was gradually added to the above solution under stirring for 30 min. After further stirring 30 min, a clear solution was obtained. Then, 2.1 g TEOS solution was added drop wise to the solution. The molar composition of the mixture was:

$$SiO_2 : 1.6\ EA : 0.215\,CTMABr : 125H_2O$$

The pH of the reaction mixture was adjusted to 8.5 by the slow addition of hydrochloric acid solution (1 M) to the mixture. At this stage, the precipitate is formed. After 2 h, under slow stirring, the precipitate was separated and washed by centrifugation. The sample was dried at 45 °C for 12 h.

Titanium-containing MCM-41 samples with different 5, 50 and 100 Si/Ti molar ratios were also prepared by a direct isomorphous substitution synthesis method. The procedure is similar to the method described above for siliceous MCM-41 but with the addition of Ti source (titanium tetraisopropoxide) in appropriate amounts. The MCM-41 and Ti–MCM-41 samples were calcined at 550 °C for 5 h to decompose the surfactants and obtain the white powder. The Ti–MCM-41 with a high content of Ti (Si/Ti ratio of 5) was used for photocatalytic experiments.

TPA–TiO_2 incorporated MCM-41 was prepared based on some modification in the described procedure previously reported in the literature [39]. 0.05 g of our prepared TPA–TiO_2 was dispersed in distilled water and a few drops of diluted HCl was added to avoid possible hydrolysis of the compound. Then 0.05 g of the calcined MCM-41 was added to make a suspension. The suspension was stirred and evaporated at 80 °C until dryness. Then the solid was ground to fine particles and dried at 200 °C for 6 h in air flowing oven. The catalyst prepared by this method was named TT–MCM-41.

Also, 0.05 g of commercial TiO_2 and 0.05 g of MCM-41 were mixed using 2 ml ethanol in agate pestle and mortar. The solvent was then removed by evaporation while mixing. Samples prepared by this method were dried at 110 °C and calcined in air at 450 °C for 6 h. This sample is designated as TiO_2/MCM-41.

2.3. Characterization and measurement methods

A Philips PW1840 X-ray diffractometer with Cu Kα radiation was used to record the powder XRD patterns. The BET specific surface area of catalysts was determined by nitrogen adsorption at liquid nitrogen temperature on a Sibata SA-1100 surface area analyzer. Elemental chemical analysis of the catalysts was done by XRF method using a Bruker, S4 Pioneer model.

The photochemical reactor was a beaker containing suspension of methylene blue (MB) solution and solid photocatalyst which was placed in a continuously ventilated chamber. The suspension was magnetically stirred before and during irradiation. UV illumination was done with a 400 W Kr lamp (Osram). The illumination power of the lamp is mainly in the UV-A region. More precisely, ≈90% of the radiated power is in the UV-A region (400–315 nm) and about 10% in the UV-B region (315–280 nm). The distance between the lamp and the reactor was 30 cm for each experiment. Prior to irradiation, the sample was stirred for 5 min to establish an adsorption–desorption equilibrium between the catalyst surface and the dye. After