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Developing a cost-effective synthesis of active iron oxide doped titania photocatalysts loaded with palladium, platinum or silver nanoparticles

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ABSTRACT

The main aim of this work is to utilize available materials such as ilmenite ore (as a source of titanium and iron oxides) and industrial wastes (as sources of noble metals) for preparation of Fe_2O_3–TiO_2 photocatalysts. A template-free one-step hydrothermal method was applied for synthesis of Fe_2O_3–TiO_2 and its loaded Pd, Pt and Ag nanoparticles. The TEM results indicated that Fe_2O_3–TiO_2 and Pd, Pt and/or Ag nanoparticles, are partly in close contact. TiO_2 nanoparticles with an average diameter of about 10 nm are quite uniform in size and shape. Pd, Pt and Ag are well dispersed and exhibit diameters of about 5, 10 and 20 nm respectively. Also, TEM evinces that the framework of the highly crystalline mesoporous Fe_2O_3–TiO_2 is composed of aligned anatase phase grown along the [1 0 1]. The N_2 isotherms of the prepared Fe_2O_3–TiO_2 and its noble metals loaded were characteristic of mesoporous solids. The meso-Fe_2O_3–TiO_2 nanocomposites possess high surface area of 175 $m^2\,g^{-1}$ and large pore volumes of 0.28 $cm^3\,g^{-1}$. These values were reduced to 124–145 $m^2\,g^{-1}$ and 0.18–0.26 $cm^3\,g^{-1}$, respectively, as a result of loading of noble metals. Photocatalytic degradation of methylene blue (MB) under UV and visible-lights indicated that the meso-Fe_2O_3–TiO_2 exhibited more enhanced activity under UV and visible-lights compared with TiO_2 P-25. Addition of Ag to Fe_2O_3–TiO_2 the most promising catalytic activity toward MB degradation under visible light. However, photodegradation of the MB under UV light was enhanced by adding Pd to Fe_2O_3–TiO_2. Utilization of raw ores and spent materials to prepare such photocatalysts represents an attractive approach due to the reduction of the production cost for practical environmental application.

1. Introduction

Photocatalysis using semiconductor particles has found increasing interest in solving global pollution problems. TiO_2 has so far been shown to be the most promising material used for both fundamental research and practical applications [1–4]. Many applications of TiO_2 nanomaterials are closely related to its optical properties. However, the highly efficient use of TiO_2 nanomaterials is sometimes prevented by its wide band gap. The band gap of bulk TiO_2 lies in the UV regime, which is only a small fraction of the sun's energy (<10%). Thus, one of the goals for improvement of the performance of TiO_2 nanomaterials is to increase their optical activity by shifting the onset of the response from the UV to the visible region [5–8]. There are several ways to achieve this goal; first, doping TiO_2 nanomaterials with other elements can narrow band gap and, thus, alter the optical properties of TiO_2 nanomaterials [3,4,9]. Second, sensitizing TiO_2 with other colorful inorganic or organic compounds can improve its optical activity in the visible light region [10]. Third, coupling collective oscillations of the electrons in the conduction band of metal nanoparticle surfaces to those in the conduction band of TiO_2 nanomaterials in metal-TiO_2 nanocomposites can improve the performance [11–14]. In addition, the modification of the TiO_2 nanomaterials surface with other semiconductors can alter the charge-transfer properties between TiO_2 and the surrounding environment, thus improving the performance of TiO_2 nanomaterials-based devices [15]. In recent years, considerable effort has been devoted to the study of Fe^{3+}-doped TiO_2 in order to improve the photocatalytic efficiency of TiO_2 [11–14]. Fe-doped nanocrystalline TiO_2 was shown to display higher photocatalytic activity with lower Fe content TiO_2 in the treatment of papermaking wastewater [16], Fe^{3+}-doped TiO_2 nanoparticles were prepared with a hydrothermal method and found that anatase, brookite, and a trace of hematite coexisted at lower pH when the Fe^{3+} content was as low as 0.5% and the distribution of Fe^{3+} was non-uniform between particles, but at higher pH, the uniform solid solution of iron-titanium oxide formed [17,18]. The generally accepted mechanism to explain this improved photocatalytic performance is the formation of shallow charge trapping

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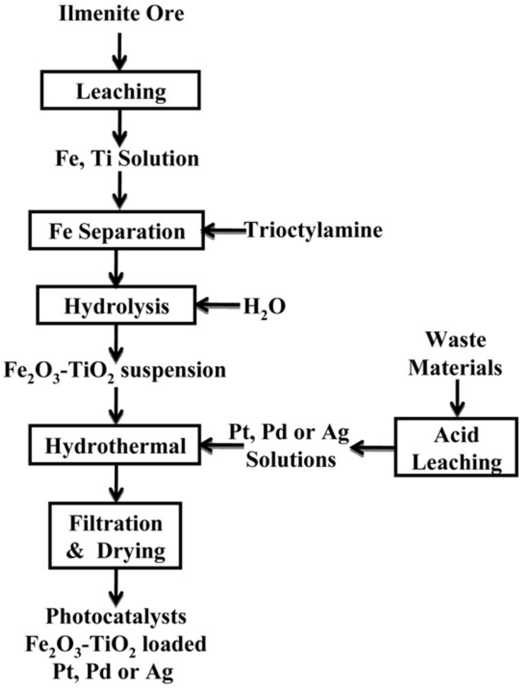

Fig. 1. Schematic flowsheet for preparation of meso-Fe_2O_3–TiO_2 photocatalysts and its loading with Pt, Pd or Ag.

sites within the TiO_2 matrix as well as on the particles' surface through the replacement of Ti^{4+} by Fe^{3+} ions [14]. Also, the presence of noble metal deposits on the TiO_2 surface can help to efficiently separate the electron hole pairs by attracting the conduction band electrons [19–23].

We have previously developed methods for acid leaching of ilmenite ore for preparation of TiO_2 [24–26]. Further, the leaching conditions with hydrochloric acid can be controlled to prepare a titanium solution that can be purified by solvent extraction to separate the contained iron. The purified ilmenite leachant contained 12 g/L Ti and 0.07 g/L Fe. This can be utilized as a source of TiO_2 and Fe_2O_3 for synthesis of meso-Fe_2O_3–TiO_2 using hydrothermal method. The aim of this work is to utilize an available material such as ilmenite ore as a source of both TiO_2 and Fe_2O_3, and spent materials as sources of noble metals for preparation of meso-Fe_2O_3–TiO_2 and its loading with Pt, Pd or Ag. The synthesized photocatalysts were evaluated for their photocatalytic activity for oxidation of MB and compared with the commercial Degussa P 25. To the best of our knowledge, this is the first report focusing on preparation of meso-Fe_2O_3–TiO_2 using the purified ilmenite leachant by hydrothermal method; such a preparation has not been reported previously.

2. Experimental

All chemicals used for synthesis and preparation (hydrochloric acid, 37%, nitric acid, 65%, hydrogen peroxide, 50%, formic acid 99% and sodium hydroxide 99.8%) were of analytical grade. Trioctylamine (Merck) was used after dilution with xylene (Nasr Co. for chemicals, Egypt) for solvent extraction of iron from ilmenite leachant. Methylene Blue (MB), Aldrich, has been used as a probe molecule in the photocatalytic tests.

2.1. Preparation of TiO_2 particles from raw ilmenite ore

A schematic flowsheet for preparation of Fe_2O_3–TiO_2 photocatalysts and its loading wit Pt, Pd or Ag is shown in Fig. 1. A representative sample of 10 kg ilmenite ore from Abu Ghalaga region, Red Sea, Egypt, was thoroughly mixed, crushed and ground to 100% −75 μm and used for preparation of TiO_2. Acid leaching of ilmenite ore was carried out using a 250 cm^3 three necked glass reactor provided with a reflux condenser and a mechanical agitator. A 200 cm^3 20% (v/v) hydrochloric acid was heated to 70 °C in the glass reactor using a thermostatically controlled glycerol/water bath. Then, a 20 g ground ilmenite ore was added and the mixture was stirred for 3 h at 400 rpm and 70 °C. The slurry was filtered off and the un-dissolved solids were thoroughly washed with 10 cm^3 3% HCl. The produced ilmenite leachant was found contained 21 g/L Ti and 36.4 g/L Fe. To achieve the oxidation of Fe^{2+} to Fe^{3+}, the ilmenite leachant was diluted with 20 cm^3 distilled water and 20 cm^3 nitric acid was added then the mixture was boiled for 15 min. This solution was purified to separate most of the contained iron by solvent extraction with trioctylamine (TOA) [26]. Equal volumes (250 cm^3 each) of the oxidized ilmenite leachant and 30% (v/v) TOA in xylene were mixed for 30 min using magnetic stirrer at 400 rpm and 30 °C. After settling the loaded organic phase was separated and the contained iron was stripped by mixing with slightly acidified water at pH 3. The refreshed organic solution was then used again for purification of the oxidized ilmenite leachant. This purification procedure was repeated three times. The produced ilmenite leachant was found containing 12 g/L Ti and 0.07 g/L Fe. The latter solution was hydrolyzed by adding 20 cm^3 of it to 200 cm^3 boiling water, and the mixture was stirred at boiling condition under reflux for 1 h. The contained Ti and Fe ions were precipitated as fine white particles suspended in the solution. This suspension was found stable over months.

2.2. Preparation of meso-Fe_2O_3–TiO_2

A 75 cm^3 of the above suspension was adapted at pH 7 by NaOH [5 M]. This was heated at 150 °C in a Teflon autoclave vessel for 8 h. The product was filtered off, washed with 100 cm^3distilled water and dried at 105 °C for 24 h to obtain the meso-Fe_2O_3–TiO_2.

2.3. Preparation of platinum and palladium solutions from waste materials

A platinum solution was prepared by dissolving platinum containing waste dust collected from ammonia oxidation reactor in Kima Company for Fertilizers, Aswan, Egypt. A 5 g of the dust was mixed with 50 cm^3 freshly prepared aqua regia and the mixture was boiled under reflux for 2 h and then the un-dissolved solids were separated by filtration. The obtained solution was found containing 1.05 g/L Pt. A palladium solution was prepared from a spent Pd/Al_2O_3 catalyst collected from Kima Company for Fertilizers, Aswan, Egypt. The spent catalyst was originally used for de-oxygenation during production of hydrogen. Palladium was leached using a solution contains 7% HCl and 5% H_2O_2 at 60 °C for 2 h with a liquid/solid ratio of 10/1. The produced solution was found containing 0.304 g/L Pd.

2.4. Preparation of platinum, palladium and silver loaded – Fe_2O_3–TiO_2

A 0.5% Pt loaded Fe_2O_3–TiO_2 was prepared as follows: a 75 cm^3 Ti and Fe ions suspension was mixed with 0.7 cm^3 platinum solution and 3 cm^3 formic acid and the pH was adjusted to 7 using 5 M NaOH solution. This mixture was heated at 150 °C in a Teflon autoclave vessel for 8 h. The grey product was filtered off, washed with 100 cm^3distilled water and dried at 105 °C for 24 h. The same procedures were used for preparation of a 0.5% Pd doped TiO_2 and 0.5% Ag loaded Fe_2O_3–TiO_2 but with adding the adequate volumes of Pd