



New porous titanium–niobium oxide for photocatalytic degradation of bromocresol green dye in aqueous solution



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ARTICLE INFO

Article history:

Received 20 March 2013

Received in revised form 6 June 2013

Accepted 9 June 2013

Available online 18 June 2013

Keywords:

A. Structural materials

A. Oxide

C. X-ray diffraction

D. Catalytic properties

ABSTRACT

In this study, high surface area semiconductors, non porous and porous titanium–niobium oxides derived from KTiNbO_5 were synthesized, characterized and developed for their utility as photocatalysts for decontamination with sunlight. These materials were then used in the photocatalytic degradation of bromocresol green dye (BG) in aqueous solution using UV light and their catalytic activities were evaluated at various pHs. For all catalysts, the photocatalytic degradation of BG was most efficient in acidic solutions. Results show that the new porous oxides have large porous and high surface areas and high catalytic activity. A topotactic dehydration treatment greatly improves catalyst performance at various pHs. Stability and long term activity of porous materials (topo and non-topo) in photocatalysis reactions was also tested. These results suggest that the new materials can be used to efficiently purify contaminated water.

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1. Introduction

Water pollution is one of the most serious human health and environmental problems. In the world, industry is one of the biggest sources of pollution, accounting for more than half the volume of all water contamination and for the most deadly pollutants. For example, dye pollutants produced by textile industries have become a major source of environmental contamination [1–3]. When contamination reaches underground water tables, it is difficult to correct pollutants which spread over wide areas [4]. Major water clean-up efforts include treatment of natural waters and sewage treatment plants as inputs to city water supplies. Many pollutants, such as halogenated hydrocarbons and pesticides, can be persistent in the environment and are hazardous with chronic exposure at ppm and ppb concentrations [5].

There are many processes and technologies available at the present time for water treatment of polluted water. Physical and chemical methods include the use of anion exchange resins [6], flotation [7], ozonation [8,9], electroflotation, electrochemical destruction, irradiation [10], adsorption [11], filtration and the use

of activated carbon [12]. The photo-Fenton reaction is also used, but it is based on the production of hydroxyl radicals using hydrogen peroxide and the iron $2^+/3^+$ redox couple [13,14]. The biological processes are less expensive and use lower energy in comparison with the chemical and physical techniques, but take longer time to complete. The use of physical and chemical treatments techniques in the industry is not widely implemented due to high toxicity and cost considerations [15,16].

Heterogeneous photocatalysis appear as an emerging destructive technology among the new oxidation methods or advanced oxidation processes. This technology leads to the total mineralization of most of the organic pollutants. UV light chemically activates photocatalysts which are wide band gap semiconductor metal oxides. It has been shown that they increase the oxidation rates of water-borne contaminants [2,12,17–19]. In the last decade, the use of TiO_2 as a photocatalyst in the treatment of wastewater has achieved great attention [20]. Pollutants are degraded under irradiation with UV light when TiO_2 is present. The problem with this material is that the powder remains suspended in water, which in turn clogs filters. The use of filters or other methods to remove TiO_2 from the treated water has proved to be inefficient and costly [21].

Porous metal oxides made up of titanium and niobium metal oxide such as HTiNbO_5 with a wide band gap can be separated easily from solution, and therefore prevent the problems of nanocrystalline TiO_2 . This is a key factor for designing a new

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low-cost, large scale photocatalytic process. As a result, novel photocatalysts, self-cleaning materials, are suitable for the treatment of drinking water and industrial wastewater [22]. In the presence of these metal oxides, the reaction at standard conditions (room temperature, atmospheric pressure) is quite fast. They are effective in full mineralization of organic contaminants in water and a wide spectrum of organic contaminants can be converted to water and CO₂.

Stability and long term activity of HTiNbO₅ porous material in photocatalysis reactions was tested. A photocatalyst should be resistive to photocorrosion, capable of advancing reactions proficiently upon repetitive use, and stable under different reaction conditions. TiO₂ has been widely used in photoreactions because it is one of the few catalysts that have been found to meet the above criteria [22]. Yu and Savage assessed the activity of TiO₂ in phenol degradation over TiO₂. The experiments were conducted using the same TiO₂ catalyst in the reactor for over 120 h. The catalyst was retrieved at the end of the tests. For the 120 h run, there was no loss in the activity of the TiO₂ catalyst [23].

Previously, the synthesis of large-pore transition metal oxides via traditional low-temperature routes has resulted in poor thermal stability, due to the materials' tendency to change from their amorphous states to crystalline solids during heating. These changes often result in pore collapse, loss of structural integrity and diminished surface areas. Using lamellar particle colloids, a method has been developed to make crystalline, large-pore Ti and Nb mixed oxide semiconductor materials with high thermal stability. These new porous oxide materials, or POX, have improved 3D electronic conduction compared to layered and nano particular semiconductors.

The nanostructure porous HTiNbO₅ prepared in this work is of highly photooxidative activity, stable phase at high temperatures, large surface area and highly photocatalytic activity, but with a strong pH dependence on the photo efficiency. In a previous study preliminary photolysis tests were done to investigate the catalytic characteristics and suitability of a porous oxide semiconductor catalyst intended for the use in photolytic water decontamination systems [24]. These results suggest that elimination of the ion exchange character of the catalyst may greatly improve its performance at various pHs. The goal of this research is to develop and explore high surface area porous material as a photocatalyst in the decontamination of water with organic material and study the effects of a topotactic dehydration reaction on this new porous material catalyst.

2. Experimental methods and materials

2.1. Synthesis of parent (KTiNbO₅) and acid exchanged (HTiNbO₅) materials

All water used was purified and deionized using microfiltration technologies. All chemicals used for experiments were bought from GFS Chemicals (Powell, OH, USA) or as indicated. According to published procedures [25–27] KTiNbO₅ parent materials were synthesized using a stoichiometric amounts of K₂CO₃ (5 mol% excess), TiO₂, and Nb₂O₅. These compounds were ground into fine powders and mixed thoroughly. The mixture was then heated in air in a programmable box furnace (Lindberg/Blue M–Asheville, NC, USA) at 1050 °C in an alumina crucible for 10 h. Synthesis of the HTiNbO₅ was accomplished via cation exchange reactions in strong acid solutions, which involves stirring powdered KTiNbO₅ in 3–4 M HCl (Fisher Scientific) solutions for 4 days and refreshing the acid solutions every day. The HTiNbO₅ solid product was rinsed twice with water and placed into a glass Petri dish and dried at room temperature. Both KTiNbO₅ and HTiNbO₅ have been characterized by TEM, SEM, XRD, and BET techniques.

2.2. Synthesis of the porous metal oxide HTiNbO₅

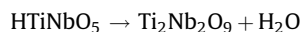
To prepare the porous metal oxide HTiNbO₅ material, the acid exchanged HTiNbO₅ was exfoliated by stirring about 2 g of this material in 100 mL of water and adding a solution of 40% tetrabutylammonium hydroxide drop wise until the resulting colloid of exfoliated sheets was stable at pH 9 [25–27].

Colloids of (TiNbO₅)_n⁻, exfoliated sheets derived from HTiNbO₅ were precipitated into porous solids by an acid vapor diffusion precipitation method. This was accomplished by mixing 4.0 mL of a colloid stock solution (0.0276 g/mL pH 10) with 20 mL of ethanol (96%). The diluted colloid was contained in an open vial and was placed in a 1000 mL covered beaker. In the same 1000 mL covered beaker 2 mL of concentrated HCl was placed. The resulting precipitated was left undisturbed for 2 days.

To dry the sample, a solvent exchange has taken place followed by CO₂ supercritical point drying. The water/alcohol was replaced by acetone prior to the drying process using series of solvent exchange steps. The beaker was covered tightly with parafilm and a rubber band to protect diffusing moisture into vials. Every two days acetone was replaced with a fresh solvent. It was repeated three times without heat. After that the vials were placed in a warm beaker (heated at 40 °C) containing dried molecular sieves or zeolite beads (dried at 280 °C) full of acetone for two days covered with aluminum foil to remove the remaining water. Then the acetone was displaced by liquid CO₂ as part of the drying process. The supercritical point CO₂ drying process allows samples to be dried without surface tension problems, which can crush porous materials during drying. The dried product is called the “non-topo” material.

2.3. Synthesis of the “topo” porous material (Ti₂Nb₂O₉)

A topotactic dehydration reaction was followed by heating the dry porous material catalyst at 450 °C for 2 h in a high temperature furnace. This “locked-in” the structure by creating covalent bonding where ionic bonds once were and eliminating the ion exchange capacity of the non-topo materials.



2.4. Characterization and analytical measurement

The morphology of the material was analyzed by a scanning electron microscope (SEM) Hitachi S-4800, Japan at 20 and 10 kV. Transmission electron microscopy (TEM) was performed on a Zeiss EM-10 microscope, Oberkochen, Germany at 60 kV. The structures of solids were analyzed by powder X-ray diffraction (XRD) at room temperature with a Bruker D8 Discover, Germany using Cu Kα radiation scanning 2θ angles ranging from 5° to 80°. Photophysical properties of the catalysts were measured using a reflectance UV–vis scanning spectrophotometer Shimadzu, Kyoto, Japan in the range of 200–550 nm. BET (Brunauer–Emmett–Teller) surface areas and pore volumes of the supported catalyst powders were determined using a Micromeritics ASAP 2020 (Georgia, USA) nitrogen gas adsorption analyzer.

2.5. Photocatalysis experiments

The experimental system consisted of a 25 mm diameter quartz cell with a 60 mL capacity. A Penray Hg light bulb ((UV pen lamp, Origin model 3SC-9, rated 5.4 mW/cm²@19 mm@254 nm, UVP LLC, USA) was used to irradiate the samples at a distance of 23 mm (outer surface of bulb to surface of quartz vessel). The amount of UV reach to the sample was measured with light power meter (PM

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