



Gold-titania/protonated zeolite nanocomposite photocatalysts for methyl orange degradation under ultraviolet and visible irradiation



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ABSTRACT

Gold-titania/protonated zeolite (Au–TiO₂/HZSM-5) composite photocatalysts were prepared via the sol–gel and impregnation processing. The structural features of the photocatalysts were investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), and ultraviolet visible diffuse reflection spectroscopy (UV–vis); the adsorption and photo-degradation of Methyl Orange (MO) were studied in the aqueous solution. The results showed that the nanoAu particles were incorporated in TiO₂/HZSM-5. The introduction of Au particles not only maintained the adsorption capacity of photocatalysts, but also promoted the photodegradation efficiency of Methyl Orange (MO). The effects of Au content, TiO₂ content, catalyst amount and calcination temperature were examined and the repeatability of photocatalytic activity was also tested. Moreover, the Methyl Orange (MO) photodegradation activity of 0.32%Au–25%TiO₂/HZSM-5 nanocomposites is the best. A plausible mechanism is proposed for the route of degradation.

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1. Introduction

Energy and environmental issues at a global level are receiving more and more attention. Therefore, tremendous studies have been made to abate environment pollution and explore renewable energy resources. During the past decades, heterogeneous photocatalysis based on TiO₂ has attracted extensive attention because of its application in the elimination of wastewater [1–4]. Indeed, TiO₂ showed good aspects for its efficiency and low cost. However, fast charge carrier recombination, low interfacial charge-transfer rate and the fatal disadvantage of TiO₂ in its large band gap (~3.2 eV) make it only absorb a small UV fraction (about 5%) of solar spectrum [5,6]. To overcome

these problems, one of the methods which have been applied to improve the photocatalytic efficiency of TiO₂ under visible light is its doping by noble metals (e.g. Pd, Au and Ag) [7–9]. The loading of a noble metal on the surface of TiO₂ can improve the photocatalytic properties in two aspects. On the one hand, the deposited noble metal can act as an electron trap aiding electron–hole separation and thus improving the quantum yield [10–12]. On the other hand, the surface plasmon resonance (SPR) effect, defined as the collective coherent oscillation of the free electrons on noble metal nanostructure induced by visible light irradiation, can enhance the localized electric field in the proximity of the metal particles, whereas the interaction of localized electric fields with a neighboring semiconductor allows for the facile formation of electron–hole pairs in the near-surface region of the semiconductor [13–16].

TiO₂ nanostructure plays an important role in photocatalytic degradation activity [17]. The dispersion of TiO₂ on solid supports is to make TiO₂ in fine particles and to

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help on concentrating pollutants to the photocatalyst surface [18,19]. Zeolites, among various supports, are considered to be important owing to their high surface area, high thermal stability and eco-friendly nature. Moreover, zeolites possess specific photophysical properties such as the control of charge transfer and electron transfer processes [20]. Recently, some research works have revealed several zeolites such as HZSM-5, Y-zeolite, H-mordenite, and mesoporous Al-MCM-41 which are successful supports for titanium dioxide [21–24]. Among zeolites mentioned above, ZSM-5 zeolite, with highly ordered micropores, surface acidity, and ion-exchange capacities, is one of the most widely applied inorganic support, adsorbent, and molecular-sized space for various photochemical reactions [25,26].

In the present study, we pay close attention to the photocatalytic decomposition of Methyl Orange over Au-TiO₂/HZSM-5 nanocomposite photocatalysts which are prepared by using the sol-gel technique and impregnation process under UV and Vis light. X-ray diffraction (XRD), surface area (BET) measurements, UV-vis diffuse reflectance spectra (UV-vis DRS), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) techniques were used for the characterizations of photocatalysts. The preparation method is novel and nanocomposite photocatalysts have never been reported previously. The nanocomposite photocatalysts show high photodegradation efficiency of Methyl Orange and good reusable performances. In addition, a photocatalytic mechanism is postulated for the Methyl Orange degradation process.

2. Experimental section

2.1. Materials

Nano-sized NaZSM-5 (SiO₂/Al₂O₃=28.6 (mol), crystal size ~50 nm, S_{BET}=350 m²/g) was hydrothermally synthesized in the presence of n-butylamine template. Before used as a support, the as-synthesized zeolitic material was subjected to, firstly, a temperature-programmed calcination in a muffle furnace in the presence of air to remove the organic template, then H⁺ exchanges were repeated twice in a solution of 0.6 M HNO₃ (ambient condition, 1 h for each time, solid-liquid ratio=1:10, g/mL), and finally drying (383 K, overnight) and calcination (813 K, 3 h) treatments were performed to obtain protonic acid nano-HZSM-5 (SiO₂/Al₂O₃=30 (mol), and S_{BET}=362 m²/g). Chloroauric acid tetrahydrate (AuCl₃·HCl·4 H₂O), titanium tetrabutoxide ([CH₃(CH₂)O]₄·Ti), ethanol (EtOH), isopropyl alcohol (C₃H₈O), and Methyl Orange (C₁₄H₁₄N₃NaO₃S) were used as provided by the suppliers without further purification [27].

2.2. Preparation of photocatalyst

The dispersion of TiO₂ and Au onto nano-sized HZSM-5 zeolitic supports was performed according to the sol-gel and impregnation process, respectively. A certain amount of titanium tetrabutoxide ([CH₃(CH₂)O]₄·Ti) was added into 30 mL absolute ethanol with 4 mL isopropanol

stabilizer as solution A. A certain amount of chloroauric acid was added to 20 mL absolute ethanol as solution B. Solution B was added to solution A with a peristaltic pump which can be set at a certain number of impregnation rate. The nano-sized zeolite HZSM-5 with saturated water quantity in its micropores was put into solution A under continuous magnetic stirring for 4 h at ambient conditions. Water consumed by the hydrolysis of titanium tetrabutoxide ([CH₃(CH₂)O]₄·Ti) was supplied by the pre-absorbed water in the micropores of the nano-sized zeolite. In this way the hydrolysis of titanium tetrabutoxide ([CH₃(CH₂)O]₄·Ti) and the subsequent sol-gel process of TiO₂ were slowed down by the slow release of H₂O from the zeolitic micropores, which was expected to be helpful for inhibiting the excessive aggregation of TiO₂ gel particles. The solid product was recovered by plain sedimentation. It was dried at 353 K overnight, and calcined in muffle furnace at 813 K for 3 h, and the Au-TiO₂/HZSM-5 composite photocatalysts were obtained.

2.3. Characterization techniques

X-ray powder diffraction (XRD) patterns of the HZSM-5 and supported catalysts were recorded on a SHIMADZU XRD-6100 diffract meter using Cu/K α radiation ($k=1.54$ Å) operating at 40 kV and 40 mA and scanning rate of 5°/min. The nitrogen adsorption/desorption isotherm was obtained at liquid nitrogen temperature 77 K by using Quanta chrome Autosorb NOVA 2200e volumetric analyzer. The specific surface areas were determined by using multi-point BET analysis. Fourier transform infrared (FTIR) spectra were recorded with a resolution of 4 cm⁻¹ in the region of 400–4000 cm⁻¹ using a spectrum One-B FTIR spectrometer with KBr pellets (Perkin Elmer, USA). Diffuse reflectance UV-vis spectra were acquired on a Cary 100 Conc (VARIAN, USA). Transmission electron microscopy (TEM) images were obtained on JEM-2000EX (JEOL, Japan). X-ray photoelectron spectroscopy (XPS) measurement was performed on a Thermo ESCALAB 250Xi with monochromatized Al/K α $h\nu=1486.6$ eV source. The likely charging of samples was corrected by setting the binding energy of the adventitious carbon (C_{1s}) to 284.8 eV.

2.4. Photocatalytic experiments

The photocatalytic degradation of Methyl Orange was carried out in a glass photoreactor. The reaction equipment was installed in an isolated cabin. The temperature of the reactor was controlled at 298 K by a water jacket [28]. A 160 W homemade high pressure mercury lamp (365 nm) was employed as the ultraviolet light irradiation source or 160 W mercury tungsten blended lamp (546.1 nm) as the visible light irradiation source. The lamp was placed 5 cm beside the profile of Methyl Orange solution. Then 0.5 g photocatalyst was suspended in 50 mL Methyl Orange aqueous solution (the ratio of solution to photocatalyst was fixed at 100/1 (ml/g)). Under continuous magnetic agitation, one hour's dark adsorption of Methyl Orange on photocatalyst was allowed to ensure the adsorption equilibrium of Methyl Orange on the photocatalyst being reached, and then the ultraviolet light irradiation or the

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