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Original Research Article

Highly Efficient Degradation of MTBE by γ-Al_2O_3/NiO/TiO_2 Core -shell Nanocomposite under Visible Light Irradiation

Golsa Iraji, Mohammad Hadi Givianrad*, Mohammad Saber-Tehrani

Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran

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ABSTRACT

γ-Al2O3/ NiO/ TiO2 as a novel photocatalyst that is active in visible light was synthesized by a simple sol-gel method. The prepared samples were characterized by XRD, DRS-UV/Vis, and TEM analysis. The photocatalytic effect of synthesized samples was examined on methyl tert-butyl ether (as a model hazardous contaminant) degradation. Experimental condition including pH, irradiation time, and photocatalyst mass were optimized. Overall, the UV/Vis spectrophotometry results indicated that the synthesized nanoparticles have an extraordinary photocatalytic activity for the degradation of methyl tert-butyl ether under visible light.

Keywords: photodegradation, nanocomposite, core-shell, titanium dioxide, methyl tert-butyl ether

***Corresponding Author: Tel.: 09109927600**
OR 09352357794 E-mail: Dr. givianrad@gmail.com

Introduction

Since 1979, methyl tert-butyl ether (MTBE) has been used commercially as an octane enhancer to replace tetraethyl lead in fuel. For a long time it has been the favorite gasoline oxygenate, mainly because of its numerous desirable properties, such as the high octane rating, low cost and favorable transfer and blending characteristics. The major environmental concern stems from its high water solubility. MTBE has been found in the environment, especially in groundwater, as a result of fuel spills, and leaks from gasoline storage tanks and pipelines [1, 2]. Accordingly, it seems that there is a need for an efficient system to remove these pollutants from aquatic environments. Semiconductor photocatalysts are also among the most reliable advanced oxidation processes designed to eliminate water soluble pollutants [3, 4]. As one of the existing semiconductor photocatalysts, TiO_2 is the most reliable solution for removing organic pollutants owing to its efficiency, nontoxicity, durability, low cost, high oxidation potential, and ease of storage. However, the wide band gap of TiO2 (3.2 eV for the anatase phase) and the high rate of electron-hole recombination are the pitfalls of the extensive usage of this valuable substance in the visible spectrum [5, 6]. Various methods of overcoming these weaknesses and limitations of TiO_2 have been analyzed [7]. One of these effective methods involves the doping and codoping of metals and nonmetals, which can reduce the band gap energy in TiO_2 by creating defects in the TiO_2 crystalline structure [8, 9]. Moreover, another effective method of reinforcing the photocatalytic effect increases the active site on the TiO_2 surface by combining it with other semiconductors [10, 11]. In the present study, γ-Al_2O_3/ NiO/ TiO_2 photocatalysts were synthesized by sol-gel method and then characterized. They were also studied and examined concerning the MTBE degradation under purple LED light [12]. To the best of our knowledge, this is the first study investigating the photocatalytic degradation of MTBE using γ-Al_2O_3/ NiO/ TiO_2 nanocomposites. The results indicated that the synthesized nanoparticles have an extraordinary photocatalytic property to remove the MTBE in aqueous solutions under visible light irradiation.

Experimental

Catalyst preparation

All the chemicals were purchased from Merck and used with no extra purification. The synthesis of the nanoparticles was carried out via the sol-gel technique. As a precursor, Tetrabutyl orthotitanate (TBOT) was applied for Titania. Further, TBOT (5 mL), absolute ethanol (20 mL), and acetyl acetone (5 mL) were mixed and blended by a magnetic mixer for 30 min to prepare the sol solution. Afterward, deionized water (4 mL) was poured into the mixture and agitated continuously for a further 10 min. Then, concentrated HCl was used to adjust pH at around 1.8. NiO and γ-Al_2O_3 were used to enhance the photocatalytic activity of TiO_2 under visible lights with a wavelength over 400 nm. The solution was subjected to mixing for 2 h. The resultant sol solution was left in the air in a dark setting for 24 h to achieve the gel. The prepared gel was then dehydrated in an oven (80 °C) for 4 h. The dehydrated sample was calcinated in a furnace at 500 °C during 2 h. Finally, the powdered nanoparticles were all formed in the anatase phase.

Characterization

The X-ray diffraction (XRD) pattern of the prepared catalyst was obtained by a Seifert 3003 PTS X-ray diffractometer using Cu Kα radiation as the X-ray source in 2θ range of 20-80°. The average crystallite size of anatase phase was obtained according to Scherrer equation. The Transmission electron microscopy (TEM) images were conducted using a Philips CM30 at 150 KV. (DRS-UV/Vis) spectra of the prepared photocatalysts were prepared by Avantes Avaspec-2048-TEC spectrophotometer. Finally, the concentrations of the solutions were analyzed by Varian Cary 300 UV/Vis spectrophotometer [13].

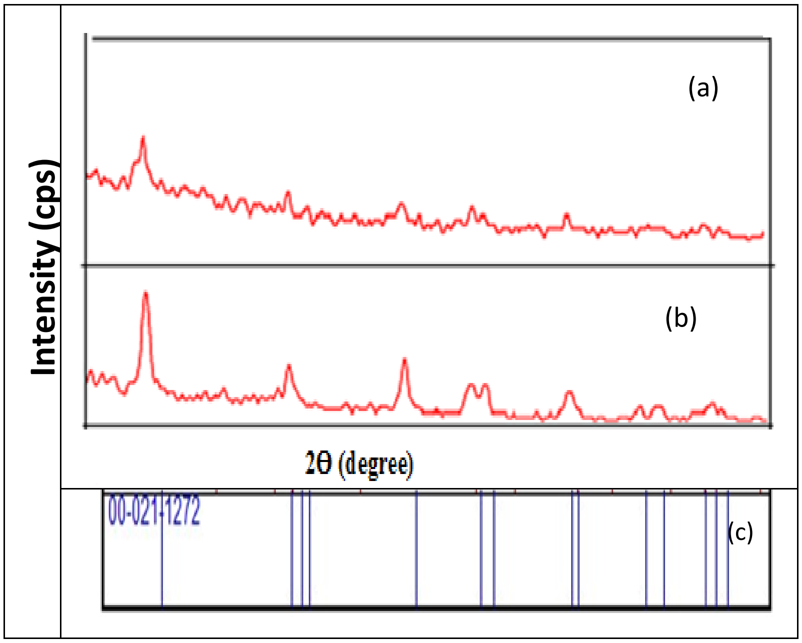

Figure. 1. XRD pattern of (a) γ-Al_2O_3/ NiO/ TiO_2 (b) TiO_2 (C) TiO_2 anatase phase standard peaks

TEM analysis

The TEM images of the samples are presented in Fig. 2. The particle sizes of γ-Al_2O_3/ NiO/ TiO_2 and TiO_2 was discovered to be around 20-25 and 24-30 nm, respectively, which confirm XRD results. A core-shell structure with a core of γ-Al_2O_3 (black) and TiO_2/NiO shell (bright) can be observed in this figure.

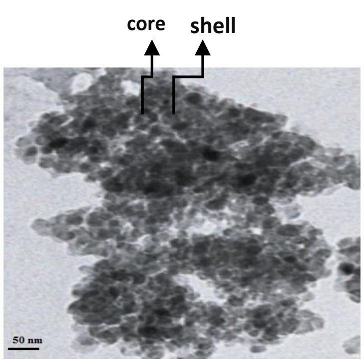

Figure. 2. TEM images of γ-Al_2O_3/ NiO/ TiO_2

UV-Vis DRS analysis

Diffuse reflectance spectra analysis of the prepared samples is demonstrated in Fig. 3. The energy band gap of each sample was obtained based on the following equation:

$$E_g = \frac{1240}{\lambda_g} \qquad (2)$$

Where Eg is the band gap energy of catalysts and λ is the wavelength at the overlap of the vertical and horizontal portions of the spectra [14, 15]. As it was described, the values of Eg for the TiO and γ-Al_2O_3/ NiO/TiO_2 were 3.20, and 2.95 eV, respectively.

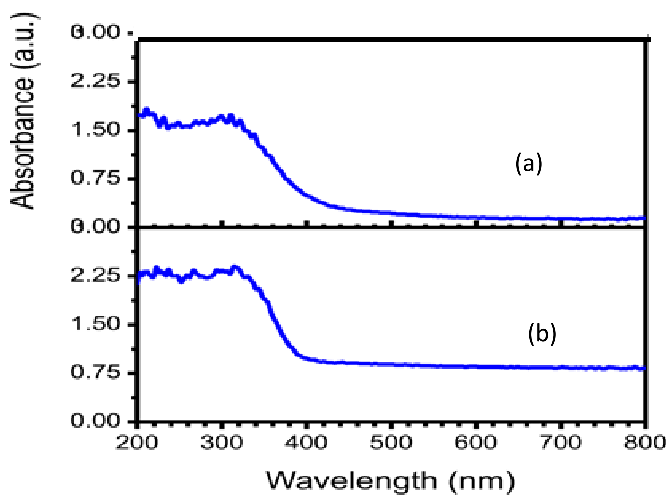

Figure. 3. DRS spectra of γ-Al_2O_3/ NiO/ TiO_2 (a), and TiO_2 (b)

Photocatalytic activities

It is believed that organic compounds such as MTBE to be destroyed through direct oxidation by the trapped holes or being attracted by hydroxyl groups. Then, the degradation rate of MTBE, was used to quantify the photocatalytic activities of γ-Al_2O_3/ NiO/ TiO_2 and calculated using the following equation

$$D\% = \frac{A_0 - A_t}{A_t} \quad (3)$$

That A_0 is the light absorbance of MTBE before the irradiation and A_t is the light absorbance of MTBE after the irradiation. Experimental condition including pH, MTBE concentration, irradiation time, and photocatalyst mass were optimized. The most degradation efficiency was obtained in acidic pH. The MTBE removal efficiency of 90.43% was obtained by 0.2 g of the photocatalyst after 198 min in 100 ml of 20 mgL^{-1} methyl tert-butyl ether solution in acidic pH of 4.25. Within the alkaline ranges of pH, the pollutant absorption rate declined because of OH ions having a great challenge to reach MTBE molecules on the nanocomposite surface. The degradation efficiency was decreased in MTBE concentrations above of 50 mgL^{-1}.

Conclusion

A sol-gel method was successfully employed to prepare novel γ-Al_2O_3/ NiO/ TiO_2 nanocomposite. The photocatalytic effect of the prepared samples was investigated by removing MTBE from the aqueous solution. The optimum values for the maximum efficiency were obtained at pH of 4.25, catalyst mass of 0.2 g, MTBE concentration of 20 mg L^{-1}, and irradiation time of 198 min. At these optimum conditions, the maximum photocatalytic degradation percentage of DF obtained was 90.43 %.

The findings suggested that the pH is the main factor affecting the degradation efficiency followed by irradiation time, MTBE concentration, and photocatalyst mass. Further, pH and concentration of MTBE on the one hand, and irradiation time and photocatalyst mass on the other hand influenced negatively and positively the MTBE degradation rate, respectively. Furthermore, a high reuse capacity without losing efficiency was established within four repetitious experiments by the reuse of the photocatalyst. Given the promising consequence of this research, a novel study is to be undertaken on the use of γ-Al_2O_3/NiO/TiO_2 for the degradation of MTBE in aqueous solution by visible light irradiation.

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