



King Saud University

Journal of Saudi Chemical Society

www.ksu.edu.sa
www.sciencedirect.com


ORIGINAL ARTICLE

Photocatalytic degradation of benzothiophene and dibenzothiophene using supported gold nanoparticle


 Suzan Khayyat ^{a,*}, L. Selva Roselin ^b
^a Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia

^b Faculty of Science and Arts in Rabigh, King Abdulaziz University, Jeddah, Saudi Arabia

Received 30 June 2016; revised 30 October 2016; accepted 2 November 2016

Available online 12 November 2016

KEYWORDS

 Photocatalytic degradation;
 Benzothiophene;
 Dibenzothiophene;
 Gold catalyst;
 TiO₂

Abstract Photocatalytic oxidation of benzothiophene (BT) and dibenzothiophene (DBT) was studied over Au nanoparticles (NPs) incorporated titania (Au/TiO₂) catalyst under UV radiation using H₂O₂ as oxidant. The reaction parameters such as, catalyst weight, Au loading, calcination of Au/TiO₂ catalysts and [H₂O₂]:[DBT] mole ratio are studied. The Au/TiO₂ catalyst was synthesised by deposition–precipitation method. The catalysts were characterized by ICPAES, XRD and TEM analysis. ICP-AES analysis demonstrate that with a nominal amount of 1, 1.5, 2, 2.5 and 3 at.% of Au in a solution at pH 7, the amount of gold deposited on the TiO₂ was 0.78, 1.42, 1.92, 2.45 and 2.87 at.% respectively. The average particle size of Au in the 2 at.% Au/TiO₂ sample after drying was 3 nm and in the sample after calcination at 573 K was 5 nm. The XPS spectra of Au/TiO₂ sample demonstrate that the sample dried at 373 K contains Au⁰ and Au³⁺ and the sample after calcination at 573 K contains Au⁰ and negligible amount of Au³⁺. The photocatalysis studies show that the Au nanoparticles (NPs) incorporated titania showed higher activity for the removal of DBT compared to pure titania. The optimum Au loading in Au/TiO₂ for the photocatalytic removal of DBT was found to be 1.5 at.% Au. The Au NPs act as electron sink to enhance e⁻/h⁺ charge separation and produce number of oxidizing species, thereby increase the reaction rate. The calcined catalyst sample showed higher activity toward DBT removal compared to the uncalcined sample. This is due to the presence of metallic gold in the calcined sample, which can effectively involve in the charge separation. The optimum catalyst weight for DBT removal was found to be 0.3 g of Au/TiO₂ for 200 ml of DBT in isooctane (200 ppm S). The optimum [H₂O₂]:[DBT] molar ratio was found to be 3. Comparison of photocatalytic removal of DBT and BT showed that the removal of DBT is faster than the BT.

 © 2016 King Saud University. Production and hosting by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

* Corresponding author.

E-mail address: saekhayyat@kau.edu.sa (S. Khayyat).

Peer review under responsibility of King Saud University.

1. Introduction

The largest and most widely used source of energy in the world is the crude oil. The maximum amount of crude oil is used as transportation fuels in the form of diesel, gasoline and jet fuel. Unfortunately, such crudes contain sulfur in the form of


<http://dx.doi.org/10.1016/j.jscs.2016.11.001>

1319-6103 © 2016 King Saud University. Production and hosting by Elsevier B.V.

This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

organic sulfur compounds. Liquid fuel contains organic sulfur compounds which pollute the environment by producing SO_2 and airborne particulate during combustion. The small amount of sulfur in fuel oil may corrode the refining equipment and poison the catalyst used in the industry. Oxidation of sulfur in the air atmosphere leads to the formation of aerosol of sulfuric acid and causes acid rain [1,2]. Because of the serious consequences of burning sulfur-lading fuels, stringent regulations on the sulfur content of transportation fuels have been issued. The commercial fuel contains large ring thiophenes as a major organic compound. The deep desulfurization is now the challenge to petroleum industry. There are some general methods used to remove sulfur compounds from hydrocarbon fuels like biodegradation, selective adsorption, extractive separation, hydro-desulfurization (HDS), and oxidative desulfurization (ODS) etc [3–7]. Although catalytic hydro-desulfurization is the most used method of reducing sulfur content in petroleum fractions, it is difficult to remove the poly-aromatic refractory sulfur compounds like DBT and its alkyl derivatives [8–11]. The operation conditions result in significant increase of the operation cost. In order to meet the new sulfur specification in transportation fuel Oxidative desulfurization (ODS) is an alternative approach. But still complete degradation of these compounds are challenging. At present, the advanced oxidation technology based on photo catalysis is attracting these days. Photocatalysis has been successfully utilized for water decontamination, purification of air, destruction of micro-organism, etc. [12–15]. Recent studies have shown that the photocatalytic method is an efficient method for the degradation of thiophene and its derivatives [16–18]. Photocatalysts under light illumination of energy greater than the band gap undergo charge-transfer processes that ultimately result in oxidation of a wide variety of organic molecules. Different semiconductors are considered for their potential use as photocatalysts [19]. Among these semiconductors TiO_2 has proven to be the most suitable for widespread environmental applications due to its exceptional optical, electronic properties. In addition, TiO_2 is biologically and chemically inert; it is stable with respect to photocorrosion; and it is inexpensive. But the band gap of TiO_2 (3.0–3.2 eV) causes an absorption in the near UV region. To improve the activity of the photocatalyst, two principal strategies have been applied. On one side, the photocatalysts with enhanced activity could be obtained by improving the structural properties of the photocatalyst. Structural properties of photocatalysts which are taken into consideration include particles size, crystalline quality, morphology, specific surface area, surface state, etc. [20–22]. Proper control of these structural properties could be achieved by proper preparation method to prepare the photocatalysts at the nanoscale. The other possibility to improve the catalytic activity could be by improving the charge separation. Earlier investigations have shown that metal doping makes the wide band gap photocatalysts active in the visible region, and it also minimizes the charge recombination, thereby increases the reaction rate [23]. Noble metal deposits on TiO_2 surface often enhance the photocatalytic reactivity because they trap CB electrons with reducing charge pair recombination and promoting interfacial electron transfer [24]. Among various noble metals, gold has attracted many researchers and are successfully utilized for the degradation of several organic compounds [25–29] as well as for disinfection of microorganism [30], hydrogen formation [31], etc. Hence, photocatalysis is a great

challenge for the degradation of benzothiophene and dibenzothiophene at low severity conditions and this method offers high potential as a complementary process for producing deep-desulfurized light fuel. The objective of this research is to study the photocatalytic degradation of benzothiophene and dibenzothiophene in presence of Au/TiO_2 and H_2O_2 catalyst systems under UV radiation for the removal of sulfur.

2. Experimental

2.1. Chemicals

Tetrachloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.99%) that was used as a gold precursor was purchased from Alfa Aesar. TiO_2 (Degussa P25) was used as semiconductor oxide photocatalysts. Benzothiophene (99%) and dibenzothiophene (98%) purchased from Sigma–Aldrich, were used as model sulfur compounds present in fuel oil. H_2O_2 solution (30% w/w aqueous solution) was used as an oxidizing agent.

2.2. Preparation of Au/TiO_2

A series of Au NPs incorporated titania (Au/TiO_2) with 1–3 at. % Au was prepared by deposition–precipitation method [32], using tetrachloroauric acid, and TiO_2 . Typically, an aqueous solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was taken and stirred at 343 K. The pH was adjusted to pH 7 by adding 0.1 N NaOH solution. This was followed by the addition of the TiO_2 . The slurry was then aged at 343 K for 2 h. The precipitates were filtered and washed carefully until all chlorine ions were removed. The precursors were dried in drying oven at 373 K for 24 h and calcined at 573 K for 4 h.

2.3. Characterization

An inductively coupled plasma atomic emission spectroscopy (ICP-AES) was performed by Jobin Yvon JY-24 spectrometer. It was used to measure the quantity of Au in the Au/TiO_2 and Au/ZnO catalysts. About 0.02 g of catalyst was dissolved by aqua regia ($\text{HNO}_3\text{:HCl}$ in 1:3 ratio) and then microwaved for 15 min. The solution was cooled down and diluted within the detection limit of the instrument.

The BET surface area was measured by physical adsorption of N_2 at 77 K using a Micromeritics ASAP 2010 instrument. The catalyst was degassed at 423 K for 4 h to remove the adsorbed impurities before analyzing the BET measurement.

X-ray diffraction was employed to obtain information about the identity of the metal (oxide) phases present in the Au/TiO_2 catalyst. X-ray diffraction (XRD) measurement was performed using a Bruker D8A X-ray diffractometer operated at 40 kV and 30 mA using $\text{CuK}\alpha$ radiation with a wavelength of 1.5406 Å. The scanning angle was from 10 to 80° at a rate of 0.05°/s.

The transmission electron microscopy (TEM) analysis was performed on a JEOL JEM-2000FX II, the operating voltage was at 160 kV.

X-ray photoelectron spectroscopy (XPS) technique was employed to obtain the information of chemical state of Au in Au/TiO_2 catalysts. The measurements were performed by a Thermo VG Scientific Sigma Probe spectrometer equipped

Download English Version:

<https://daneshyari.com/en/article/4909346>

Download Persian Version:

<https://daneshyari.com/article/4909346>

[Daneshyari.com](https://daneshyari.com)