Journal of Sciences, Islamic Republic of Iran 25(3): 281 - 285 (2014) http://jsciences.ut.ac.ir
University of Tehran, ISSN 1016-1104

Nano- TiO2/Nd Deposited on γ-Fe2O3 as a Magnetically Separable Photocatalyst

H. Ghasemi Mobtaker*, S.J. Ahmadi, and P. Ashtari

Nuclear Fuel Cycle Research School, Nuclear Science and Technology Research Institute, Tehran, Islamic Republic of Iran

Received: 4 November 2013 / Revised: 12 July 2014 / Accepted: 4 August 2014

Abstract

TiO_2/Magnetit and TiO_2/Nd/Magnetit were prepared and used for photocatalytic decomposition of the methylorange as a pollutant. TiO_2 and TiO_2/Nd were prepared by sol gel method and were characterized using XRD, FT IR and TEM. The prepared catalysts were deposited on magnetite surface to have a catalyst with magnetite core. So the catalyst can be separated easily from the waste solution by a magnet. Comparing the photocatalytic activity of TiO_2/Magnetit and TiO_2/Nd/Magnetit showed that doping the TiO_2 by Nd increases the catalytic activity. Acidity of the waste has also promising effect on catalytic activity and the time needed for methylorange decomposition was decreased in low pHs. Complete decomposition of the methylorange was confirmed by LC MS.

Keywords: TiO_2/Magnetit, TiO_2/Nd/Magnetit, Photocatalyst, Sol gel, Methylorange.

Introduction

Organic pollutants especially azo dyes are being increased in environment because of wide use in various industries. Their toxic effects by producing aromatic amines and low degradation rate has convinced the researcher to focus on finding an efficient and low cost method for their treatment [1-4]. So many procedures have been developed to treat these pollutants, but not all of them had great efficiency and leading to full degradation. Most of them separate only the pollutant from the waste solution producing a secondary pollution [5,6]. Among them the photocatalytic degradation is a promising way to decompose the pollutant completely to minerals without any secondary waste. Electron-holes produced by UV irradiation of catalyst, forms the radicals which decompose the organic pollutant. TiO_2 as a photocatalyst has many advantages against the other catalysts and has been widely used for the purpose. Chemical stability, non toxicity, low cost and easy synthesis are some of the reasons of using widely. To increase the photocatalytic activity, TiO_2 was doped by some metals. These dopants can prevent electron-hole recombination so increasing the decomposition efficiency. Some metal ions were used as dopant in researches which have various catalytic activities [7-14]. We also have investigated the effect of TiO_2 dopping with some ions in our previous work [15]. We found that Nd-dopped TiO_2 has the maximum activity for degradation of methylorange, so we used it to prepare the deposited TiO_2/Nd on γ-Fe_2O_3.

Using TiO_2 as suspended powder led to increase its

---

* Corresponding author: Tel: +9882062386; Fax: +982188221116; Email: hosein_g@yahoo.com

activity because of large surface area, but it is problematic in industry as it needs to be separated from the solution and recycle. The separation process is a cost and time consuming process, so immobilization the catalyst can be useful in this case. As the immobilization, reduces the surface area, the catalytic activity decreases. For keeping the efficiency it is better to immobilize the catalyst on particles with small size to increase the activity. To be separated easily the catalyst from the solution, γ-Fe_2O_3 were used as a support in this work. It can be separated from the solution easily by a magnet [16-19].

The solution acidity has also significant effect on photocatalytic activity. Surface charge in various pH can alter the adsorption characteristic and so affecting the degradation rate. Protonation of the pollutant species may have also some effects on degradation rate. Solution acidity was investigated in this work to enhance the catalytic activity [20].

Materials and Methods

1. Materials

Titanium tetraisopropoxide (TTiP), Ferrous sulfate, Ferric chloride, nitric acid, absolute ethanol, methylorange and metal nitrates of the analytical grade were purchased from Merck Company. Hydroxypropyl cellulose (HPC) was purchased from Aldrich Company. Double distilled water was used for the preparation of methylorange solutions.

2. Catalyst preparation

The Nd-doped TiO_2 was synthesized using sol–gel method as following [15]: 12 g of TTiP was dissolved in 100 ml of ethanol under stirring to prepare the solution **A**. HPC was added (0.2 g) as a stabilizer. Solution **B** was prepared by adding 0.18 ml of nitric acid into 10 ml of ethanol. Solution **C** was obtained by dissolving the neodymium nitrate in ethanol. Nd^+/ Ti (IV) mole ratio was 1:500. Solution **B** was dripped into solution **A** under vigorous stirring to form a clear sol. Solution **C** was also dripped into previous solution. Then the reaction system was dispersed at ~20000 rpm for 30 minutes using a homogenizer. The sol was then placed in an ultrasonic bath for 30 minutes, aged at room temperature (25–30°C) for 48 hours to form gel, and dried at 70°C for about 24 hours to remove water and organic solvents. Finally the dried gel was calcinated in an electric furnace at 500 °C for 4 hours.

γ-Fe_2O_3 was prepared by coprecipitation of ferrous sulphate and ferric chloride by potassium hydroxide [21]. Solution of ferrous sulfate and ferric chloride (0.1 M) was prepared by adding them into 500 ml oxygen free 0.1 M hydrochloric acid. An excess potassium hydroxide solution (0.5M) was added under nitrogen bubbling and vigorous stirring until the final pH=12. Precipitate was washed by distilled water, dried and annealed at 450 °C for 30 min to form γ-Fe_2O_3. It was dispersed in water and was placed in ultrasonic bath. The pH was adjusted at 10.5 and after signification for 10 min 200 ml silicate solution (3%) was added drop by drop into the dispersion and the final pH was adjusted at 10. After 1 hour sonification and 12 hour stirring, a thin layer of silicate had been deposited on particles. It was separated, dried and annealed at 450 °C for 30 min to prepare the silica coated γ-Fe_2O_3 cores (SF). SF and Nd-doped TiO_2 were mixed and small portion of the water was added to form paste. It was then sonificated for 30 min, dried and annealed for 30 min in 500 °C to form the final photocatalyst.

3. Characterization of catalysts

The synthesized TiO_2/Nd catalysts were characterized by X-ray diffraction method using a STOE STADI MP X-ray diffractometer with Cu Kα radiation ($\lambda = 0.15406$ nm). The average size of catalyst particles was calculated approximately by Sherrer equation. TEM (Philips EM 208 S) was used to investigate the particles morphology. FT IR spectrum of the sample was obtained on a FT-IR model rector 22, Bruker, Germany. Methylorange solutions were analyzed by UV-Vis. spectrometry using a Cary UV–Vis spectrometer at the maximum absorption wavelength ($\lambda = 465$ nm). To confirm complete decomposition of methylorange at the end of degradation and detection of some intermediate species, LC-MS analysis was employed. It was done by Agilent MSD1100 equipment.

4. Photocatalytic degradation

Photocatalytic activity of the synthesized samples investigated in a 1000 cc glass photo-reactor. Methylorange solution (5 ppm) was used as a pollutant model. 1 g of catalyst was put in the reactor and 1000 cc of the solution was added. The solution was stirred by a magnet stirrer for 1 hour in darkness to determine the adsorption of the dye by the catalyst. A UV lamp (15 W) was used for irradiating the solution. Sampling (about 10 ml) was done every 15 minutes and the samples were filtered, centrifuged and analyzed by UV-Visible spectrometry. LC-Mass was used during photodegradation to analyze the intermediate production and confirm the complete decomposition of the dye.

To investigate the acidity effect on degradation process 4 solutions with the pH of 2, 4, 7 and 9 were used. The solution pH was adjusted by nitric acid and ammonia solutions.

Results and Discussion

Figure 1 shows the XRD pattern for TiO_2/Nd synthesized by sol gel method. The major phase in the synthesized sample is anatase, as the pattern confirms, but the minor phase of rutile can also be seen in the pattern. Rutile phase presence in the catalyst leads to increase the mesopority of the catalyst consequently the surface area can be increased, but the photocatalytic activity of rutile is not as high as the anatase, so the optimum case is the anatase as major phase and rutile in minor phase. Using the Sherrer equation the particle size of the catalyst was calculated about 30 nm.

Figure 2 shows the FT IR spectrum of TiO_2/Nd. The peak around 450 cm^{-1} is attributed to Ti-O band of the anatase phase. The peak seen around 1113 cm^{-1} is because of un-polymerized [SiO4] group. The bending band of the Nd-O-Ti can be seen in 1349 cm^{-1} (as a shoulder) and the peaks around 1624 cm^{-1} and 3429cm^{-1} are for bending and stretching vibrations of -OH groups.

XRD pattern of the γ-Fe_2O_3 is showed in figure 3. The vertical lines under the peaks shows the standard pattern of the γ-Fe_2O_3 which are correspond to the peak position of the prepared samples.

TEM image of the TiO_2/Nd is shown in figure 4. It shows that the size of the most particles is less than 30 nm. The particle size distribution is not in wide range.

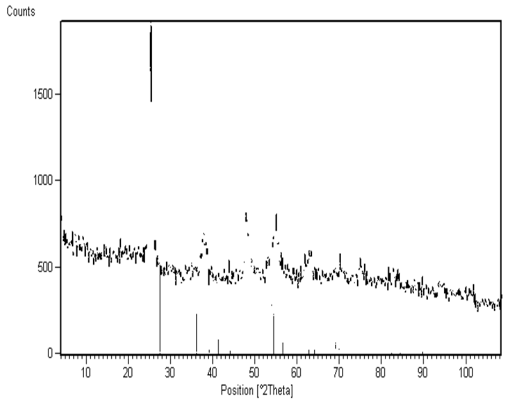

Figure 1. XRD pattern of TiO_2/Nd

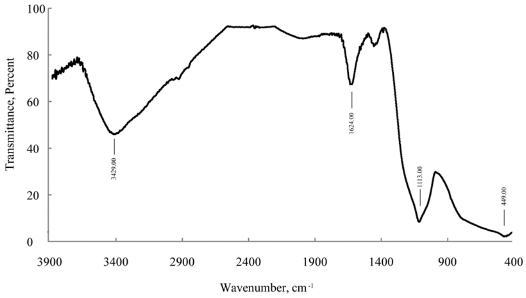

Figure 2. FT IR spectrum of the TiO_2/Nd

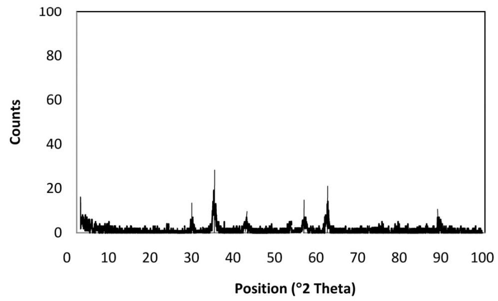

Figure 3. XRD pattern of Magnetite

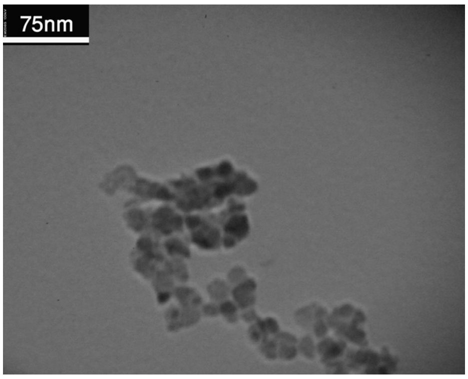

Figure 4. TEM image of the TiO_2/Nd

Two samples were prepared as photocatalyst, one was TiO_2 deposited on γ-Fe_2O_3 and the other Nd-doped TiO_2. The photocatalytic activity of the catalysts were compared in a diagram. As can be observed in figure 5 the photocatalytic activity of the TiO_2/Nd/Magnetit was higher than TiO_2/Magnetite. Nd presence as dopant in TiO_2 structure can prevent the recombination of electron and holes which are produced by UV irradiation of the catalyst surface. The electron and holes leads to radicals production which proceed the photocatalytic process. The dopants increase the catalytic activity by preventing the recombination of the electron and holes and also reducing the band gap energy in TiO_2.

It can be seen that the TiO_2/Nd/Magnetite decreases the methyorang concentration more than 98% in 250 min, but the TiO_2/Magnetit decrease the 75% of the methylorange concentration in 250 min.

To investigate the pH effect on photocatalytic activity the process was done in 4 various pH. As can be observed in figure 6 the time needed for complete degradation of the methylorange decreases by decreasing the pH. At pH= 9 the degradation in 250 min is about 65% while it is 98% at pH= 7. In lower pHs the time is less as it reaches to 75 min at pH= 2. In acidic

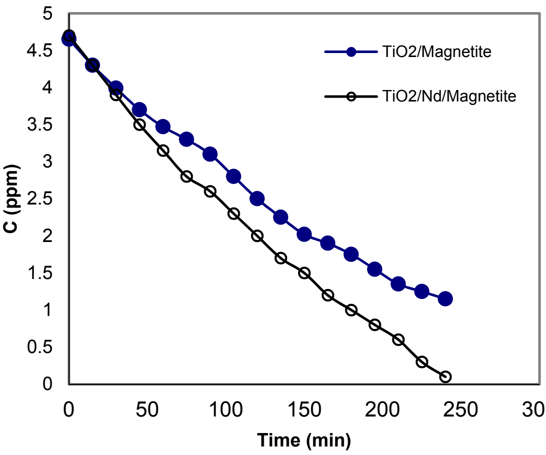

Figure 5. Comparing the photocatalytic activity of TiO2/Magnetit and TiO2/Nd/Magnetit at pH=7

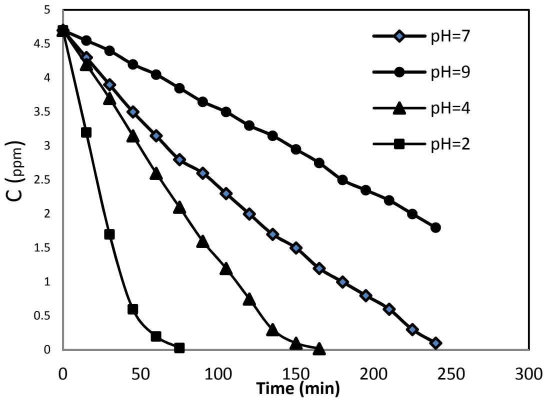

Figure 6. pH effect on degradation time by TiO2/Magnetit

media the surface of the catalyst can be charged positively, so the adsorption property of the surface towards the reacting spices can be varied. The other reason that can be mentioned for the observation is the protonation of the methylorange which can affect the decomposition reactions.

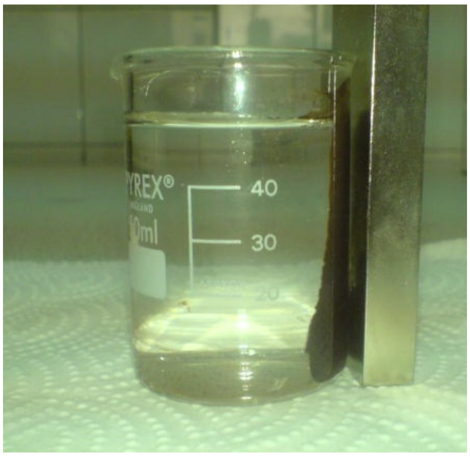

Figure 7. Catalyst separation by a magnet

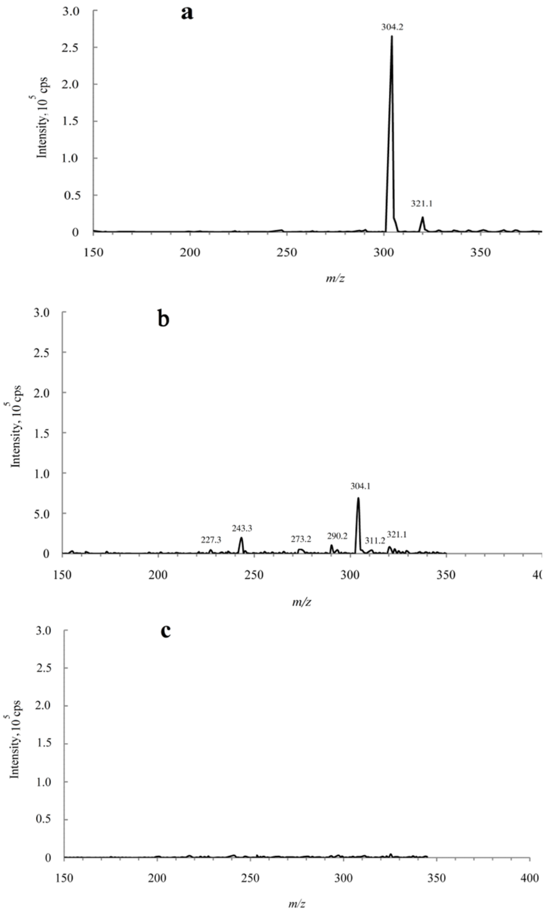

Figure 8. LC-Mass analysis of methylorange before degradation (a), after 60 min (b) and after degradation (c) by TiO2/Nd/Magnetit at pH=7

The most important goal of the present work was to prepare a catalyst that can be separated easily from the waste solution. Using the catalyst in suspension mode has the advantage of great surface area which leads to high catalytic activity, but the catalyst separation from the waste is a big deal. Figure 7 shows that the prepared catalyst can be separated easily by a magnet and reused in other batch.

LC MS analysis was used to detect the fragments of methylorange which are formed by radical attacks before complete degradation and also to confirm the complete decomposition at the end of process. Discoloration of methylorange occurs before complete decomposition. Figure 8 shows the results for various times. It can be seen in that there is only methylorange peak before degradation (a); fragmentation of methyorange is observed after 60 minutes and there is a lot of fragment in solution (b); and finally at the end of the process (c) there is no fragment with considerable concentration which confirms the complete decomposition of the methyorange

Conclusion

In this research TiO_2/Magnetit and TiO_2/Nd/ Magnetit were used for photocatalytic decomposition of the methylorange.Various characterization methods such as XRD, FT IR and TEM confirmed its structure. The magnetite core led to easy and fast separation of catalyst from the liquid waste. Comparing the photocatalytic activity of TiO_2/Magnetit and TiO_2/Nd/ Magnetit showed that doping the TiO_2 by Nd increases the catalytic activity. Acidity of the waste has also promising effect on catalytic activity and the time needed for methylorange decomposition was decreased in low pHs. It can be because of protonation of methylorange and also the effect of acidity on catalyst surface. LC MS analysis was used to confirm decomposition of the methylorange to water and carbon dioxide. It was shown that complete degradation was done by the method. This method is limited to dilute solutions and in solution with a lot of colloidal particles it has low efficiency.

References

1. Wuyou F., Haibin Y., Lianxia C., Hari B. , Minghua L., Guangtian Z., Anatase TiO_2 nanolayer coating on strontium ferrite nanoparticles for magnetic photocatalyst, *Colloids and Surfaces A*: *Physicochem. Eng. Aspects*, **289**: 47–52 (2006).
2. Height M. J., Pratsinis S.E., Mekasuwandumrong O., Praserthdam P., Ag–ZnO catalysts for UV-photodegradation of methylene blue, *Appl. Catal. B Environ*., **63**: 305–312 (2006) .
3. Sakthivel S., Neppolian B., Shankar M.V., Arabindoo B., Palanichamy M., Murugesan V., Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and TiO_2, Sol. *Energy Mater. Sol. Cells*, **77**: 65–82 (2003).
4. Mrowetz M., Selli E., Photocatalytic degradation of formic and benzoic acids and hydrogen peroxide evolution in TiO_2 and ZnO water suspensions, *J. Photochem. Photobiol. A Chem*., **180**:15–22 (2006).
5. Konstantinou I.K., Albanis T.A., TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations-A review, *Appl. Catal. B: Environ*., **49**:1–14 (2004).
6. Tang W.Z., An H., UV/TiO_2 photocatalytic oxidation of commercial dyes in aqueous solutions, *Chemosphere*., **31**: 4158–4170 (1995).
7. Chakrabarti S., Dutta B.K., Photocatalytic degradation of model textile dyes in wastewater using ZnO as semiconductor catalyst, *J. Hazard. Mater*., **B112**: 269–278 (2004).
8. Reddy M.P., Venugopal A., Subrahmanyam M., Hydroxyapatite photocatalytic degradation of calmagite (an azo dye) in aqueous suspension, *Appl. Catal. B: Environ.,* **69**: 164–170 (2007).
9. Saquiba M., Tariqa M.A., Faisala M., Muneer M., Photocatalyic degradation of two selected dye derivatives in aqueous suspensions of titanium dioxide, *Desalination*, **219**: 301–311 (2008).
10. Silva C.G., Wang W., Faria J.L., Photocatalytic and photochemical degradation of mono-, di- and tri-azo dyes in aqueous solution under UV irradiation, *J. Photochem. Photobiol. A: Chem*., **181**: 314–324 (2006).
11. Stylidi M., Kondarides D.I., Verykios X.E., Visible light-induced photocatalytic degradation of Acid Orange 7 in aqueous TiO_2 suspensions*, Appl. Catal. B: Environ.,* **47**:189–201 (2004).
12. Su C., Hong B.Y., Tseng C.M., Sol–gel preparation and photocatalysis of titanium dioxide*, Catal. Today*, **96**: 119–126 (2004).
13. Sun J., Wang X., Sun J., Sun R., Sun S., Qiao L., Photocatalytic degradation and kinetics of Orange G using nano-sized Sn (IV)/TiO_2/AC photocatalyst, *J. Mol. Catal. A: Chem*., **260**: 241–246 (2006).
14. Liu G., Wu T., Zhao J., Photo-assisted degradation of dye pollutants. 8. Irreversible degradation of Alizarin Red under visible light radiation in air-equilibrated aqueous TiO_2 dispersions, *Environ. Sci. Technol*., **33**: 2081-2087 (1999).
15. Moradi SH., Ghasemi Mobtaker H., Ahmadi S. J., Investigation of Coupled System Effect on Photacatalytic Activity of TiO_2/M Nano Composite, *Fresen. Environ. Bull.,* **21**(12a): 3874-3880 (2012).
16. Watson S., Beydoun D., Amal R., Synthesis of a novel magnetic photocatalyst by direct deposition of nanosized TiO_2 crystals onto a magnetic core, *J. Photochem. Photobiolo. A,***148**: 303–313 (2002).
17. Yuan G., Baohua C., Hulin L., Yongxiang M., Preparation and characterization of a magnetically separated photocatalyst and its catalytic properties Materials, *Chem. Phys.,* **80**: 348–355 (2003).
18. Kurinobu S., Tsurusaki K., Natui Y., Kimata M., Hasegaw M., Decomposition of pollutants in wastewater using magnetic, photocatalyst particles, *J. Mag. Mag. Mate.,* **310**: e1025–e1027 (2007).
19. Watson S., Beydoun D., Amal R., Synthesis of a novel magnetic photocatalyst by direct deposition ofnanosized TiO_2 crystals onto a magnetic core, *J. Photoch. Photobio. A,* **148**: 303–313 (2002).
20. Ioannis K. K., Triantafyllos A. A., TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations A review, *App. Catal. B: Environ.,* **49**: 1–14(2004).
21. Chen, F., Xie, Y., Zhao, J., Lu, G., Photocatalytic degradation of dyes on a magnetically separated photocatalyst under visible and UV irradiation, *Chemosphere*, **44**:1159-1168 (2001).