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UV Photocatalytic Degradation of Toluene and Tetradecane Using Anatase TiO₂ Crystals.

Saleh Nasser Al-Busafi*, Khaled Melghit, and Kawakob N Al-Dughaishi.

Department of Chemistry, College of Science, Sultan Qaboos University, Box 36, Al-Khodh 123, Oman.

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*For Correspondence

Department of Chemistry,
College of Science, Sultan
Qaboos University, Box 36, Al-
Khodh 123, Oman.
Tel: 00-968-24142305
Fax: 00-968-24141469

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ABSTRACT

Crystalline titanium oxide was obtained by simple and low cost method. X-ray diffraction (XRD) measurements confirmed that the prepared TiO₂ catalyst has a single anatase structure with no indication of the presence of a secondary phase. Transmission electron microscopy (TEM) micrograph demonstrates that the anatase TiO₂ has spherical homogenous crystals with average diameter of 1.10 nm. Toluene and tetradecane adsorbed on the surface of titanium oxide were easily degraded when exposed to UV light. The % removals of toluene and tetradecane at 120 minutes were 84.5 and 98.8 respectively.

INTRODUCTION

Using semiconductors to activate photocatalysis of organic compounds becomes the most attractive method for decomposition of toxic pollutants to non-hazardous substances [1-4]. Titanium dioxide (TiO₂) has proved to be the best catalyst, among other semiconductors, used in photocatalysis purification process of environmentally harmful pollutants [5-9]. This can be attributed to its fundamental properties such as stability, availability, and its photogenerated holes are vastly oxidizing. TiO₂ has been used to degrade various organic compounds like halocarbons, pesticides, chlorophenols, and congo red into safe substances such as water and carbon dioxide via irradiation with UV light [10-13].

Among the factors that influence the reactivity of TiO₂ towards photodegradation of organic compounds is its crystalline phase. It was found that anatase phase of TiO₂ (appears in the form of pyramid-like crystals) exhibits higher catalytic activity compared with the other two forms brookite and rutile [14]. Such high photocatalytic activity is related to the large surface area of the anatase phase since most catalytic reactions over heterogeneous catalysts take place on the surface of the catalysts. A mixture of anatase and rutile TiO₂ (80%:20%) was reported to degrade dodecane slowly (30% conversion at 100 minutes) [15].

Despite the vast studies appeared in literature that describe the photocatalytic activity of TiO₂, only few papers have reported the use of anatase TiO₂ for photocatalytic treatment of aliphatic and aromatic pollutants. The aim of this study is to prepare anatase TiO₂ using a simple and low cost method and to investigate the feasibility of employing it to degrade aromatic and aliphatic compounds under UV light.

EXPERIMENTAL

All chemicals were used as received without further purification. Titanium (III) chloride solution (30% w/v TiCl_3) was purchased from BDH. Toluene, tetradecane and 1-dodecanol (analytical grade) were purchased from Aldrich. Ammonium hydroxide solution (NH_4OH , 10%), H_2O_2 solution (10%), hexane, and ethyl acetate (analytical grade) were purchased from Acros Organics.

Preparation and characterization of anatase TiO_2

TiCl_3 solution (5 mL) was diluted with 45 ml distilled water and stirred for 48 h at room temperature. Ammonium hydroxide solution (25 mL) was added and the mixture was stirred for further 5 minutes. Then, H_2O_2 solution (1 mL) was added and the color of the solution changed from dark purple to yellow. After 2 hours a yellow gel formed at the bottom of the beaker. The mixture was concentrated under vacuum and the gel was washed 4 times with water. After each washing, the mixture was allowed to settle in order to allow the separation of the gel from the solution by decantation. A last wash was done by acetone in order to dry the product. The produced yellow gel was heated in an oven for 4 hours at 400 °C in order to produce anatase TiO_2 . The anatase structure of the catalyst was determined from X-ray diffraction (XRD) pattern obtained with an X-ray diffractometer (Philips 1710). The structure, shape and size of the catalyst were analyzed by using JEOL 1234 transmission electron microscope (JEOL, Tokyo, Japan).

Preparation of calibration curve of toluene

In three replicates, 10 solutions of toluene in ethyl acetate were prepared with final concentrations 11 ppm, 22 ppm, 43 ppm, 65 ppm, 87 ppm, 108 ppm, 130 ppm, 152 ppm, 174 ppm and 217 ppm. The absorbance of the samples was measured at $\lambda_{\text{max}} = 269$ nm using UV/Vis spectrophotometer (Shimadzu PC-1601, Kyoto, Japan). Plotting the concentrations verses absorbance gave linear relationship with a slope equal to the molar absorptivity (ϵ).

Photocatalytic testing of toluene and tetradecane

Photodegradation of toluene was carried in a 25 mL beaker containing 5 mg of TiO_2 and 10 ml of water. Toluene (2.3 μL) was added and the mixture was stirred under UV-lamp (50W, germicidal lamp, main wavelength 254 nm) for 5, 10, 15, 30, 60, 90, 120, 150 and 180 minutes. After each reaction, the mixture was extracted with ethyl acetate and the UV absorbance of toluene was measured at 269 nm. Same procedure was followed for tetradecane except using GC-MS (Quattro Ultima Pt tandem quadruple mass spectrometer (Waters Corp. MA, USA) instrument) as detection method in the presence of 1-dodecanol as an internal standard.

RESULTS AND DISCUSSIONS

Characterization of anatase TiO_2 crystals

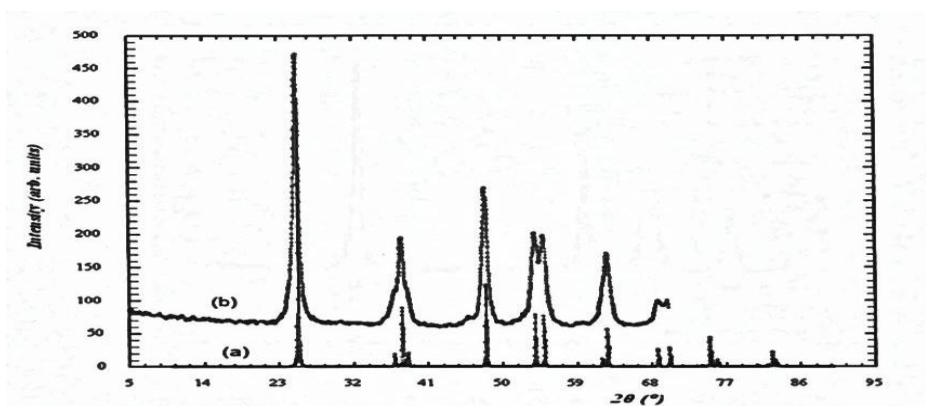


Figure 1: XRD pattern of the prepared TiO_2 catalyst (b) (for comparison, pure anatase TiO_2 XRD pattern is included)

Fig. 1 shows the X-ray (XRD) diffraction pattern of anatase TiO_2 phase obtained from heating the wet gel $\text{TiO}_2 \cdot x\text{H}_2\text{O}$ at 400 °C for four hours. The X-ray pattern shows a pure crystalline phase with all diffraction peaks identical to TiO_2 anatase structure. There were no diffraction peaks that indicate an amorphous structure. The X-ray pattern of prepared TiO_2 was compared with that of authentic sample as shown in Fig. 1. The two patterns are almost identical. Fig. 2 exhibits the X-ray diffraction pattern compared with the refined spectra of tetragonal TiO_2 with the difference curve obtained by Rietveld refinement using the FullProf program. It shows that the peaks of prepared TiO_2 are overlapping with calculated ones and give the same Bragg positions which indicate the purity of the prepared TiO_2 catalyst.

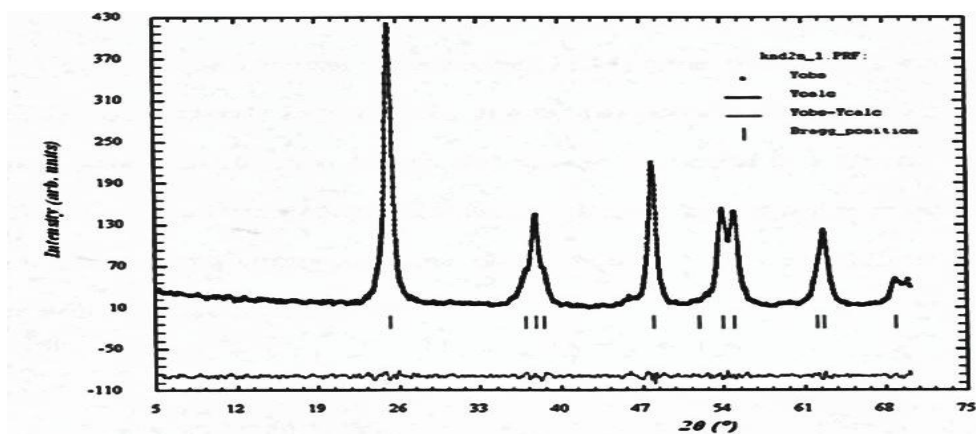


Figure 2: XRD pattern of the prepared TiO_2 compared with the refined spectra of tetragonal TiO_2 . The unit cell and its parameters of the crystal structure of the prepared TiO_2 catalyst were calculated from the obtained X-ray and compared with reported values (Table 1) [16].

Table 1: Cell parameter of TiO_2 compared with literature values [16].

Cell parameter	Prepared TiO_2	Literature values
a (Å)	3.789	3.789
b (Å)	3.789	3.789
c (Å)	9.495	9.537
α (°)	90.00	90.00
β (°)	90.00	90.00
γ (°)	90.00	90.00
Space group	$I4_1/amd$	$I4_1/amd$

Transmission electron microscopy (TEM) of TiO_2 reveals homogeneous spherical shaped crystals as shown in Fig. 3. The estimated average diameter of the spheres is 1.10 nm.

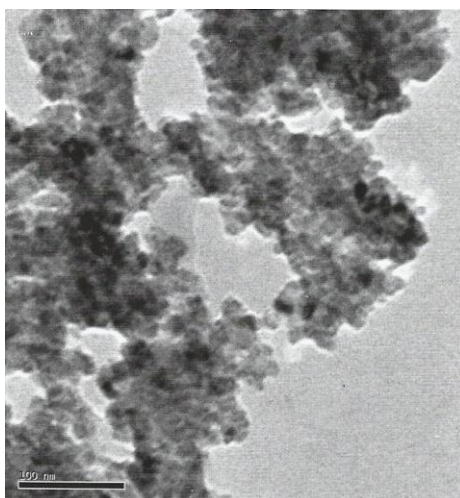


Figure 3: TEM micrographs of the prepared TiO_2 catalyst

Calibration curve of toluene

UV absorptions of 10 different concentrations of toluene in ethyl acetate were recorded at 269 nm. Plotting the concentrations versus absorbance of toluene solutions gave a linear relationship with a slope equal to molar absorptivity (ϵ) (Fig. 4). The calibration equation was $y = 263.46x + 0.018$ ($r^2 = 0.993$, uncertainty = 0.0094) for toluene.

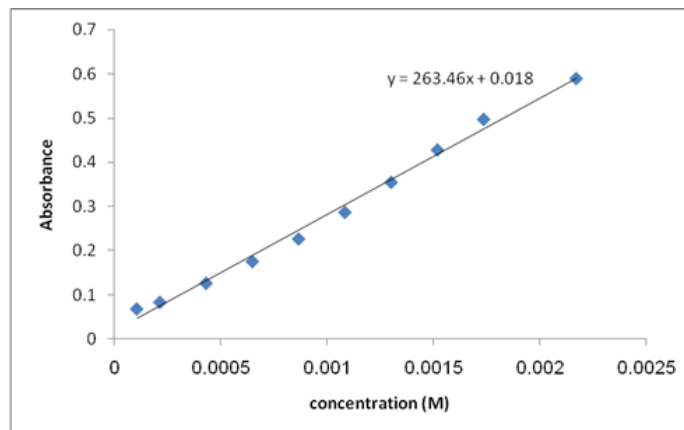


Figure 4: Absorbance versus concentration curve of toluene

Photocatalytic analysis of toluene and tetradecane

Stirred suspensions of TiO_2 (0.5 mg/mL) in water containing toluene (initial concentration 173 ppm) were irradiated at 254 nm by UV lamp. The photocatalytic activity of anatase TiO_2 was measured by calculating the percentage removal of toluene under UV light at room temperature (21 – 25 °C). The removal activity was calculated using the following equation:

$$\% \text{ removal} = \frac{[C]_{\text{initial}} - [C]_{\text{final}}}{[C]_{\text{initial}}} \times 100$$

Where $[C]_{\text{initial}}$ is the concentration of toluene at 0 time and $[C]_{\text{final}}$ is the concentration of toluene after irradiation at different times (Table 2 and Fig. 5). The conversion of 30.6% was reached after 5 minutes of irradiation then the degradation rate gradually increases with time until it reach 84.5% of conversion at 120 minutes. From 120 to 180 minutes the conversion almost remains constant. The photodegradation of tetradecane was faster than that of toluene under the same condition (Fig. 5). Upon UV irradiation 93.9% of tetradecane was degraded by TiO_2 within 30 minutes compared to only 59.9% of toluene in the same period. Almost total degradation (99.3%) of the aliphatic hydrocarbon was reached at 150 minutes of the photocatalytic reaction.

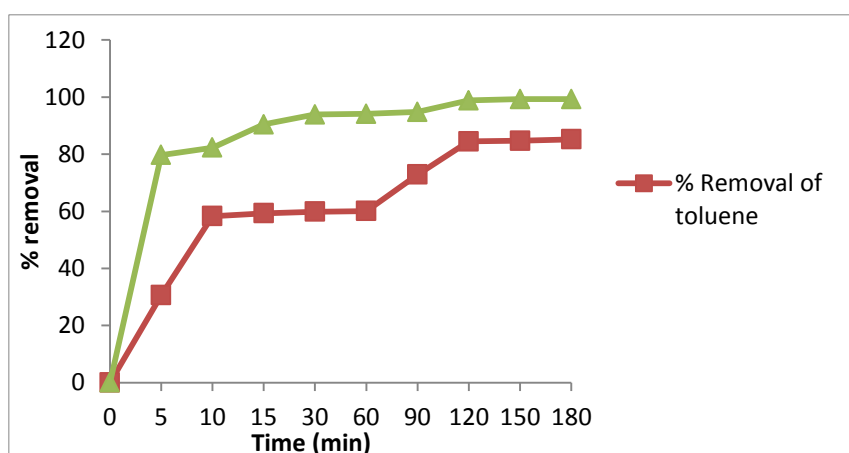


Figure 5: Percent removal efficiency of toluene and tetradecane as a function of time for anatase TiO_2 catalyst

Table 2: Degradation of toluene and tetradecane by TiO₂ under UV light.

t(min.)	% Removal of toluene	% Removal tetradecane
0	0	0
5	30.6	79.7
10	58.3	82.3
15	59.3	90.4
30	59.9	93.9
60	60.1	94.1
90	72.9	94.8
120	84.5	98.8
150	84.7	99.3
180	85.2	99.3

CONCLUSION

Anatase TiO₂ was successfully synthesized by a simple method starting from TiCl₃. The structure of the catalyst was characterized by X-ray diffraction (XRD) measurements and transmission electron microscopy (TEM). Pure anatase TiO₂ showed faster photodegradation of aliphatic hydrocarbon (tetradecane) compared with aromatic hydrocarbon (toluene) under UV light.

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REFERENCES

1. Bhatkhande DS, Pangarkar VG, Beenackers AA. *J Chem Technol Biotechnol.* 2002;77:102-116.
2. Hoffmann MR, Martin ST, Choi W, Bahnemann DW. *Chem. Rev.* 1995;95:69– 96.
3. Marin ML, Santos-Juanes L, Arques A, Amat AM, Miranda MA. *Chem Rev.* 2012;112:1710–1750.
4. Maira AJ, Lau WN, Lee CY, Yue PL, Chan CK, Yeung KL. *Chem Eng Sci.* 2003;58:959–962.
5. Fujishima A, Rao TN, Tryk DA. *J Photochem Photobiol C: Photochem Rev.* 2000;1:1–21.
6. Yao N, Yeung KL. *Chem Eng J.* 2011;167:13–21.
7. Affam AC, Chaudhuri M. *J Env Manag.* 2013;130:160.
8. Yeung KL, Leung WK, Yao N, Cao SL. *Catal Today.* 2009;143:218.
9. Linsebigler AL, Lu G, Yates JT. *Chem Rev.* 1995;95:735–758.
10. Sabate MA, Anderson H, Kikkawa M, Edwards CG, Hill J. *J Catal.* 1991;127: 167.
11. Percherancier JP, Chapelon R, Pouyet B. *J Photochem Photobiol A: Chem.* 1995;87:261.
12. D'Oliveira JC, Minero C, Pellizzetti E, Pichat P. *J Photochem Photobiol A: Chem.* 1993;72:261.
13. Melghit K, Al-Rabaniyah S. *J Photochem Photobiol A: Chem.* 2006;184:331-334.
14. Murakami HK, Kato J, Kera Y, Ohtani B. *J Phys Chem. B* 2002;106:10501–10507.
15. Sturini M, Soana F, Albinì A. *Tetrahedron.* 2002;58:2943-2950.
16. Horn M, Schwerdtfeger CF, Meagher EP. *Zeitschrift Fur Kristallographie.* 1972;136:273-281.