Vietnam Journal of Science and Technology ***57*** *(3A) (2019) 54-60*

doi:10.15625/2525-2518/57/3A/14074

HYDROGEN-PLASMA-TREATED NANO TiO_2 FOR PHOTOCATALYTIC OXIDATION OF VOCS IN AIR STREAM

Le Nguyen Quang Tu[1], Nguyen Van Dung[1], Pham Trung Kien[2],
Ca Quoc Vuong[3], Nguyen Quoc Thiet[3], Cu Thanh Son[3], Nguyen Quang Long[1, *]

[1]*Faculty of Chemical Engineering, Ho Chi Minh City University of Technology – VNU- HCM*
268 Ly Thuong Kiet, District 10, Ho Chi Minh City

[2]*Faculty of Materials Technology, Ho Chi Minh City University of Technology – VNU- HCM*
268 Ly Thuong Kiet, District 10, Ho Chi Minh City

[3]*Institute of Applied Materials Science- Vietnam Academy of Science and Technology.*
1A Thanh Loc 29, Thanh Loc, District 12, Ho Chi Minh City

[*]Email: *nqlong@hcmut.edu.vn*

Received: 31 July 2019; Accepted for publication: September 2019

Abstract. Unlike water treatment processes, the photocatalytic oxidation of VOCs in air stream exhibits many challenges. This study will develop the hydrogen-plasma-treated TiO_2 with improvement in photocatalytic activity. The hydrogen-plasma-treatment was carried out in the non-thermal atmospheric pressure reactor at room temperature. The catalysts were characterized by advanced techniques such as X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR) and N_2 adsorption at low temperature (77 K) for surface area analysis. The photocatalytic activity of the catalyst has been investigated under UV light with various relative humidity. Significantly, the conversion of toluene by a plasma-treated sample was 1.5 times higher than the non-treated TiO_2 in similar reaction condition.

Keywords: plasma, TiO_2, VOCs removal, hydrogen treatment, photocatalysis.

Classification numbers: 2.4.2, 2.6.1, 3.4.5.

1. INTRODUCTION

Volatile organic compounds (VOCs) are the potential pollutants due to their hazardous properties for environment and human. There are two major directions in treating VOCs: decomposition technology and recovery technology [1]. The photo-catalytic oxidation processes (PCO) have recently been proven to be a promising technology for VOCs removal and the reaction mechanism of photocatalytic removal of toluene, a typical VOC compound, using the common TiO_2 photocatalyst has been proposed [2-4]. The reaction of the photo-generated holes (h+) and the OH-(surface) or the adsorbed H_2O produces hydroxyl radicals (OH•), which are highly chemical active species for the toluene decomposition. Hence, the high water adsorption capacity of the photocatalysts should be desired to stably decompose the organic pollutants.

TiO_2 is currently the most efficient catalyst for PCO processes. However, it still displays some major disadvantages. In order to be widely used, it has to overcome its limited photocatalytic region ($\lambda < 400$ nm) and poor affinity towards organic pollutants. Furthermore, unlike formaldehyde or other low carbon compounds, toluene has a strong aromatic ring structure with very high structural strength. Therefore, the byproduct of the oxidation reaction can potentially occupy the reactive site of TiO_2 causing the removal efficiency to decrease over time [5]. To tackle those problems of TiO_2-based photocatalyst, the following approaches have been adopted in previous studies: (1) modification, (2) enhancing surface area, (3) doping on the additional adsorbents, etc. Recently, hydrogen TiO_2 modification processes have received a lot of attention thanks to the ability to expand the light absorption spectra of TiO_2 and enhance the existence of photoelectron and holes [6, 7]. Hydrogenated TiO_2 can be prepared through many methods such as hydrogen thermal treatment [8], chemical reduction and oxidation [9], electrochemical reduction [10], etc. In spite of the remarkable findings of this material, the equipment and the general conditions lead to high costs. Therefore, it is necessary to develop a simple method to effectively prepare this advanced TiO_2 material. The hydrogenation TiO_2 technology by plasma is known for its ability to modify TiO_2 surfaces without heat or high pressure and improving photocatalytic activity in the treatment of organic compound in the liquid phase [11].

In this study, we will prepare hydrogenated TiO_2 by hydrogen plasma treatment system, which can easily be applied to TiO_2 without annealing. This process will introduce -OH functional group on the material, which is expected to improve the catalytic activity during photo-oxidation of organic compounds in the gas phase under UV light.

2. EXPERIMENTAL AND METHOD

2.1. Material preparation and characterization

TiO_2 (P25-Degussa) purchased from Sigma-Aldrich was used in this study. Hydrogen-plasma-treated TiO_2 was prepared in plasma systems at the Institute of Applied Materials Science. The process of treating materials by plasma was carried out in a reactor made of quartz with an internal diameter of 10.6 mm, with a 1.6 mm diameter Wolfram electrode and a 1.7 mm thick dielectric layer (quartz tube). Materials before processing in plasma were dried under vacuum conditions, at a temperature of 110 °C for 2 hours. The material after drying was set inside the reactor and kept in the plasma. The material handling process was carried out in H_2/Ar gas flow (10 % v/v), at a voltage of 7 kV. The hydrogen plasma processing time was adjusted in the range of 0-60 minutes. The samples were then denoted as TiO_2-X with X = 0, 15, 30, 60 is the processing time. Determination of the bonds existing in the material before and after reduction in a plasma environment was made using Fourier infrared conversion spectra (FT-IR) performed on PerkinElmer Spectrum 10.5.2 with the wavenumbers from 4000 to 400 cm^{-1}. The crystalline structure of the above catalysts was analyzed by powder X-Ray diffraction using Bruker D2 diffractometer, with Cu Kα radiation ($\lambda = 1.54184$ Å) operated at 30 kV and 10 mA.

2.2. Measurement of photocatalytic oxidation of toluene

An annular photocatalytic reactor surrounded by four Sankyo Denki F10T8BLBs light all that emitted UV-A radiation in the 315 to 400 nm range with a wavelength of 352 nm (a UV emission capacity of 1.5 W) was used to carry out photocatalytic removal of toluene in a continuous stream. The four lamps were symmetrically located 2.5 cm far from the annular photocatalytic reactor. The surface of the inner tube of the reactor was coated with the catalyst by the spin-spray coating method [12-14]. For the photocatalytic test, a gas mixture of toluene, oxygen (99.99 %), and water vapor, and nitrogen (99.99 %) was introduced to the annular reactor. The toluene and water vapor in the mixture were generated by bubbling method and the water vapor concentration were varied in order to investigate the effect of these concentrations by controlling the mass-controllers and the liquid-bath's temperature. The toluene concentration was analyzed on-line by a Flame Ionization Detector (FID) in gas chromatography (Hewlett Packard 5890 plus) which equipped with a 6-way valve for online injection. The removal efficiency ψ (%) was calculated by the following equation:

$$\psi = (1 - A_i/A_0) \times 100\ \%$$

where: A_i: area of toluene peak at time i and A_0: area of toluene peak at initial time. In addition, before starting the photocatalytic experiment with light, the feed stream was flowed in the reactor in dark condition for saturating adsorption.

3. RESULTS AND DISCUSSION

FTIR spectra for samples of hydrogen plasma treated in TiO_2 are shown in Figure 1. FTIR spectrums of all TiO_2-X sample had a characteristic peak at about 400-800 cm^{-1}. This is a sign for bridging stretching modes of Ti-O and Ti-O-Ti in structure [15]. A wide band at 3200-3600 cm^{-1} is the primary O-H stretching of the hydroxyl functional group. At the same time, the band at about 1600 cm^{-1} is the contribution of bending vibration of the H-OH group. Therefore, plasma treatment introduced hydroxyl (-OH) functional group into TiO_2, leading to the appearance of characteristic peaks of –OH. It can also be seen that processing time contributed to the number of functional groups appearing on the material. In the first 30 minutes, the longer the treatment time, the more active sites are modified. From 30 minutes to 60 minutes, the increase in time does not change the –OH functional group. From 60 minutes onwards, the –OH groups will be separated from the material, leading to the peak intensity of –OH vibration of TiO_2-90 samples lower than the previous samples. This phenomenon occurred due to the elimination of internal hydroxyl from within the TiO_2 shell and also reported in previous study of hydrogenated TiO_2 using different methods [16-18].

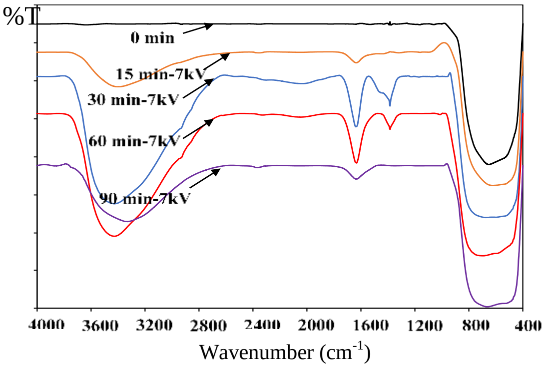

Figure 1. FTIR spectrum of hydrogenated TiO_2 samples.

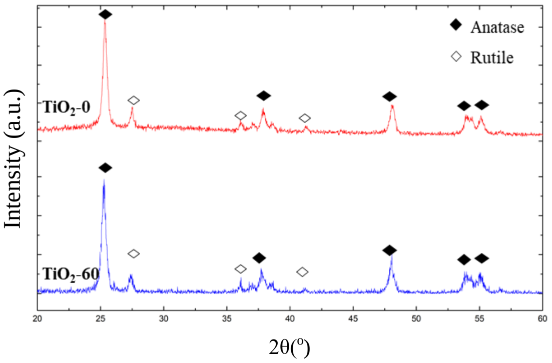

Figure 2. XRD pattern of TiO_2-0 and TiO_2-60.

The XRD patterns of the samples are shown in Figure 2. The XRD pattern of TiO_2 and TiO_2-60 exhibited peak at 25.2°; 36.8°; 37.7°; 38.5°; 48°; 53.7° and 55° which are characteristic of the anatase form in TiO_2 (JCPDS Card no. 21-1272) and at 27.8°; 36.2°; 39.8°; 41.6°; 44.8°; 55° and 57.5° which indicate the rutile form of TiO_2 (JCPDS Card no. 21-1276). The peaks have the same intensity as the standard sample TiO_2 (P25 Degussa) in [19-22], indicating no denaturation after preparation. The acuteness of peaks in the XRD pattern demonstrates high crystallinity of sample.

The process of plasma treatment altered the surface of TiO_2, from which it can possibly alter toluene adsorption capacity as well as the competitiveness of water molecules in the environment. To examine this hypothesis, the specific surface area was determined using NOVA 2200e, Quantachrome Instruments and the result are given in the following Table 1.

Table 1. Specific surface area.

Sample	**Surface area BET (m^2/g)**
TiO_2-0	50.9
TiO_2-60	51.2

Furthermore, the investigation of toluene adsorption capacity of the catalyst samples was carried out in two relative humidity of 60 % (Figure 3-a) and 20 % (Figure 3-b). First, from N_2 adsorption result, the surface area of TiO_2 was not much affected by plasma treatment. Second, the toluene removal efficiency by adsorption between treated samples and TiO_2-0 is similar. However, when the moisture content decreases, the adsorption capacity is slightly improved. With less water molecules to compete, TiO_2 samples were able to remove more toluene by adsorption.

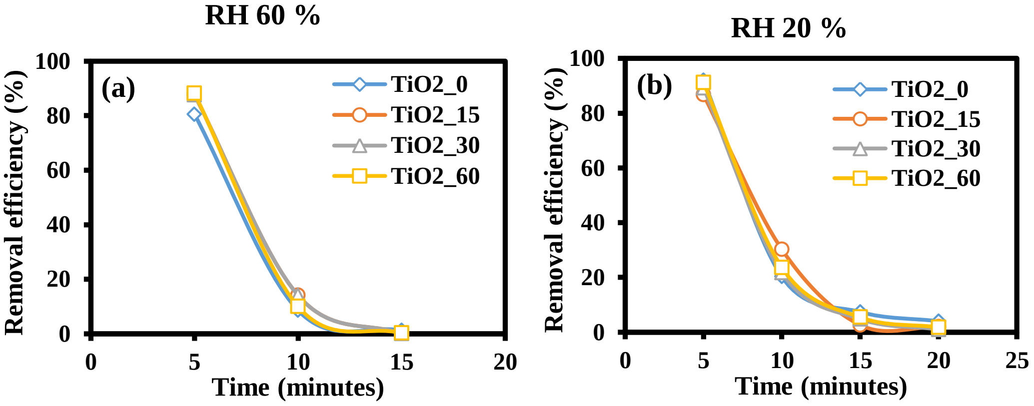

Figure 3. Toluene dynamic adsorption of the catalysts under two humid conditions (C_{tol} = 314 ppm_v, F = 50 mL/min, C_{O2} = 20 v%, T = 39 °C, $m_{cat.}$= 0.2 g).

In the investigation of the effect of surface plasma processing time at the relative humidity 60 % (Figure 4-a), all samples reached the highest conversion efficiency value after the first 10 minutes and these values differed. The oxidation efficiency was 65.94 %, 54.05 % and 52.85 %, corresponding to TiO_2-15, TiO_2-30 and TiO_2-60, respectively. It can be seen that the prolonged plasma time will reduce catalytic activity. However, all catalytic samples lost their activity over time. After 60 minutes of the experiment, only about 20 % of toluene was decomposed due to photocatalytic oxidation. The samples were also investigated under relative humidity of 20 % (Figure 4-b). Surprisingly, the change in humidity has only a small effect on the oxidation rate and the trend of the samples is to reach the highest value in the 10th minute and then lose its activity over time. This can be explained by the presence of the -OH group on the surface of the material. These groups can easily form free hydroxyl radicals to react with toluene in the absence of water molecules in the surrounding environment. In addition, the performance of TiO_2-60 sample was also improved.

As mentioned above, changing the humidity only have a small effect on the catalytic activity of the TiO_2 catalytic samples treated with plasma. However, TiO_2-0 is greatly influenced by the lack of water molecules. This can be observed from the results of investigating of toluene oxidation shown in Figure 5. It can be seen that, due to the absence of water molecules, TiO_2-0 could not generate enough free hydroxyl radicals to oxidize toluene. Therefore, only about 40 % of toluene was degraded at the time of the highest performance of the catalyst. Meanwhile, samples treated with plasma treated had higher activity. The -OH groups on the surface of plasma-treated TiO_2 can easily convert to radicals and promote the oxidation reaction despite of the low water content. Significantly, the conversion of TiO_2-15 samples is 1.5 times higher than TiO_2-0 in this condition.

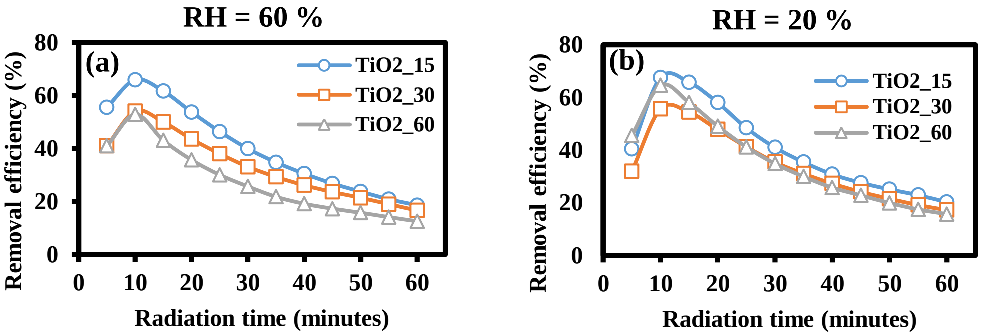

Figure 4. Toluene removal by plasma-treated TiO_2 catalysts at two humidity conditions. (C_{tol} = 314 ppm_v, F = 50 mL/min, C_{O2} = 20 v%, T = 39 ^oC, $m_{cat.}$= 0.2 g).

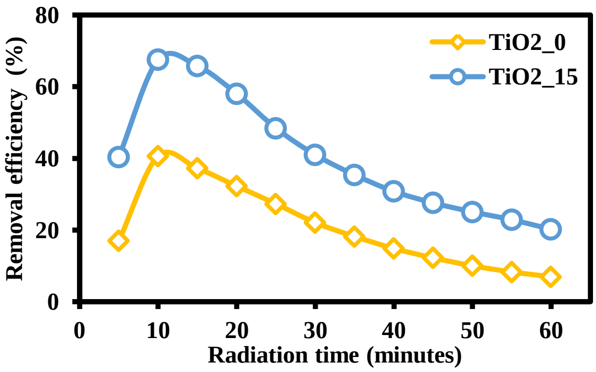

Figure 5. Photocatalytic toluene removal efficiency of non-hydrogenated and hydrogenated TiO_2. (C_{tol} = 314 ppm_v, RH = 20 %, F = 50 mL/min, C_{O2} = 20 v%, T = 39 ^oC, $m_{cat.}$= 0.2 g).

4. CONCLUSIONS

The process of non-thermal atmospheric hydrogen plasma treating is simple and easy to implement and does not change the phase of the material. By applying this process, -OH species were introduced to the surface of TiO_2. FTIR spectra had confirmed the existence of -OH species in TiO_2. Toluene adsorption capacity between materials before and after modifying was the same. Notably, the ability of toluene oxidation in low humidity conditions is significantly improved. The results also showed that, under the selected conditions to perform plasma treatment, the TiO_2-15 exhibited better result than non-hydrogenated TiO_2. In spite of increasing catalytic activity, the catalyst was slowly deactivated over time. Therefore, it is necessary to incorporate some other research to completely improve the catalytic activity.

Notation

C_{tol}	concentration of toluene, ppm_v
C_{O2}	concentration of oxy, v%
F	feed stream, mL/min
T	temperature, ^oC
m_{cat}	catalyst’s weight, g
RH	relative humidity, %.

REFERENCES

1. Khan F. I. and Ghoshal A. K. - Removal of Volatile Organic Compounds from polluted air, Journal of Loss Prevention in the Process Industries **13** (6) (2000) 527-545.
2. Bianchi C. L., Gatto S., Pirola C., Naldoni A., Di Michele A., Cerrato G., and Capucci V. - Photocatalytic degradation of acetone, acetaldehyde and toluene in gas-phase: comparison between nano and micro-sized TiO2, Applied Catalysis B: Environmental **146** (2014) 123-130.
3. Ismail A. A., Abdelfattah I., Atitar M. F., Robben L., Bouzid H., Al-Sayari S. A., and Bahnemann D. W. - Photocatalytic degradation of imazapyr using mesoporous Al2O3–TiO2 nanocomposites, Separation and Purification Technology **145** (2015) 147-153.
4. Shiraishi F., Maruoka D., and Tanoue Y. - A better UV light and TiO2-PET sheet arrangement for enhancing photocatalytic decomposition of volatile organic compounds, Separation and Purification Technology **175** (2017) 185-193.
5. Dong H., Zeng G., Tang L., Fan C., Zhang C., He X., and He Y. - An overview on limitations of TiO2-based particles for photocatalytic degradation of organic pollutants and the corresponding countermeasures, Water Research **79** (2015) 128-146.
6. Zheng Z., Huang B., Lu J., Wang Z., Qin X., Zhang X., Dai Y., and Whangbo M.-H. - Hydrogenated titania: synergy of surface modification and morphology improvement for enhanced photocatalytic activity, Chemical Communications **48** (46) (2012) 5733-5735.
7. Pesci F. M., Wang G., Klug D. R., Li Y., and Cowan A. J. - Efficient suppression of electron–hole recombination in oxygen-deficient hydrogen-treated TiO2 nanowires for photoelectrochemical water splitting, The Journal of Physical Chemistry C **117** (48) (2013) 25837-25844.
8. Liu N., Schneider C., Freitag D., Hartmann M., Venkatesan U., Müller J., Spiecker E., and Schmuki P. - Black TiO2 nanotubes: cocatalyst-free open-circuit hydrogen generation, Nano letters **14** (6) (2014) 3309-3313.

9. Wang Z., Yang C., Lin T., Yin H., Chen P., Wan D., Xu F., Huang F., Lin J., and Xie X. - Visible-light photocatalytic, solar thermal and photoelectrochemical properties of aluminium-reduced black titania, Energy & Environmental Science **6** (10) (2013) 3007-3014.
10. Xu C., Song Y., Lu L., Cheng C., Liu D., Fang X., Chen X., Zhu X., and Li D. - Electrochemically hydrogenated TiO 2 nanotubes with improved photoelectrochemical water splitting performance, Nanoscale research letters **8** (1) (2013) 391.
11. An H.-R., Park S. Y., Kim H., Lee C. Y., Choi S., Lee S. C., Seo S., Park E. C., Oh Y.-K., and Song C.-G. - Advanced nanoporous TiO 2 photocatalysts by hydrogen plasma for efficient solar-light photocatalytic application, Scientific reports **6** (2016) 29683.
12. Byrne J. A., Eggins B. R., Brown N. M. D., McKinney B., and Rouse M. - Immobilisation of TiO2 powder for the treatment of polluted water, Applied Catalysis B :Environmental **17** (1998) 25-36.
13. Pawlowski L. - Finely grained nanometric and submicrometric coatings by thermal spraying: A review, Surface & Coatings Technology **202** (2008) 4318-4328.
14. Yasumori A., Yanagida S., and Sawada J. - Preparation of a Titania/X-Zeolite/Porous Glass Composite Photocatalyst Using Hydrothermal and Drop Coating Processes, Molecules **20** (2) (2015) 2349-2363.
15. Martins N. C., Ângelo J., Girão A. V., Trindade T., Andrade L., and Mendes A. - N-doped carbon quantum dots/TiO2 composite with improved photocatalytic activity, Applied Catalysis B: Environmental **193** (2016) 67-74.
16. Yu X., Kim B., and Kim Y. K. - Highly enhanced photoactivity of anatase TiO2 nanocrystals by controlled hydrogenation-induced surface defects, ACS Catalysis **3** (11) (2013) 2479-2486.
17. Yan Y., Han M., Konkin A., Koppe T., Wang D., Andreu T., Chen G., Vetter U., Morante J. R., and Schaaf P. - Slightly hydrogenated TiO_2 with enhanced photocatalytic performance, Journal of Materials Chemistry A **2** (32) (2014) 12708-12716.
18. Leshuk T., Parviz R., Everett P., Krishnakumar H., Varin R. A., and Gu F. - Photocatalytic activity of hydrogenated TiO2, ACS applied materials & interfaces **5** (6) (2013) 1892-1895.
19. Kulkarni R., Malladi R., Hanagadakar M., Doddamani M., Santhakumari B., and Kulkarni S. - Ru–TiO 2 semiconducting nanoparticles for the photo-catalytic degradation of bromothymol blue, Journal of Materials Science: Materials in Electronics **27** (12) (2016) 13065-13074.
20. Jalali J., Mozammel M., and OjaghiIlkhchi M. - Photodegradation of organic dye using co-doped Ag/Cu TiO 2 nanoparticles: synthesis and characterization, Journal of Materials Science: Materials in Electronics **28** (22) (2017) 16776-16787.
21. White L., Koo Y., Yun Y., and Sankar J. - TiO2 Deposition on AZ31 Magnesium Alloy Using Plasma Electrolytic Oxidation, Journal of Nanomaterials (2013).
22. Jalali J. and Mozammel M. - Degradation of water-soluble methyl orange in visible light with the use of silver and copper co-doped TiO 2 nanoparticles, Journal of Materials Science: Materials in Electronics **28** (7) (2017) 5336-5343.