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Photocatalytic removal of VOCs in humid condition using Pd/TiO_2 coated annular photocatalytic reactor

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ABSTRACT

This study reports preparation, characterization and photocatalytic activity of nano Pd/TiO_2 catalyst for removal of VOCs in humid conditions. Different Pd/TiO_2 samples were prepared with Pd content ranging from 0.3 to 1wt%. Wet impregnation and metal-sol were applied for Pd/TiO_2 preparation. The catalysts were used in a coated annular photocatalytic reactor for removal of VOCs in highly humid condition by a photocatalytic process. By this photocatalytic process, the maximum toluene removal efficiency was 63% (wet impregnation) and 85% (sol-metal) in the case of initial toluene concentration of 314 ppm and relative humidity of 60%.

Introduction

Volatile organic compounds (VOCs) are defined as "any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions" by U.S. Environmental Protection Agency [1]. VOCs are not only dangerous to human health but also harmful to the environment because most of them are toxic and can cause serious environmental problems such as greenhouse effect, photochemical smog, stratospheric ozone depletion etc [2, 3]. VOCs came from cooking and tobacco smoke, building materials, furnishings, dry cleaning agents, paints, glues, cosmetics, textiles, plastics, polishes, disinfectants, house-hold insecticides, and combustion sources [4–7]. Obviously modern society cannot avoid them, therefore an effective method to eliminate VOCs from the air that people breathe is urgently needed. The VOCs treatment methods are mainly divided into two major directions: decomposition technology and recovery technology. For recovery technology, adsorption, absorption and condensation wereused. In decomposition, VOCs has been removed by thermal oxidation, biological filtration method or photocatalytic oxidation. VOCs treatment with cost-effective and environmentally-friendly technologies is the race of scientists in the world. Photocatalytic oxidation is a suitable method for removing volatile organic compounds at low concentrations with many advantages. In order to achieve high efficiency in VOCs treatment, different approaches have been adopted to promote photocatalytic activity of TiO_2, modified by precious metals such as Au, Pt, Pd,...[8, 9]. The addition of platinum to the TiO_2 catalyst improves considerably its performance for the photocatalytic oxidation of different organic chemicals [4-8]. Electronic transport

through the Schottky barrier formed in the metal–semiconductor interface could account for this beneficial effect, since the electrons transferred to the metal particles can favor reduction reactions on their surface and prevent hole–electron recombination [8]. Other precious metals of the platinum group like palladium are also effective catalysts for VOC's combustion [10]. However, Pd-supported photocatalysts has been scarcely studied and exclusively in reactions in aqueous solutions [7, 12, 13]. Nevertheless, Pd/TiO_2 is a potentially interesting catalyst for the elimination of air pollutants, as palladium can promote effectively the photoactivity of titanium dioxide [6, 7, 12, 13]. In the present work, we explore the feasibility of using Pd/TiO_2 for the photocatalytic oxidation of toluene as a typical aromatic VOCs, and formadehyde, a common indoor VOCs.

Experimental

A series of highly disperse materials Pd/TiO_2 were synthesized by two different ways to study the effects of preparation methods on the photocatalytic activity: wet impregnation method and metal sol method [14].In the first synthesis method, the appropriate amounts of TiO_2 (Degussa P25 Germany) were dispersed into 50 ml of C_2H_5OH 99.5 wt% (VN-Chemsol Co., Ltd.), stirred in 30 mins at 400 rpm at ambient temperature and pressure. Then, the solutions of $PdCl_2$ 2.81 g/L (Merck, Germany) were added gradually with the flowrate of 1 ml/minute into prepared solutions. To minimize the effect of acidity to the photocatalytic properties of TiO_2, pH of these solutions was adjusted to the value of 5.5, and the final solutions were continuously stirred in 2 hours at the same above conditions. After that, all solvent was removed under vacuum condition (0.2 bar gauge) at 80˚C. The raw materials after the solvent evaporating completely were dried overnight at 80˚C. Finally, calcination in inner atmosphere (nitrogen) was applied in 4 hours. The amounts of TiO_2 and $PdCl_2$ 2.81 g/L solutions were calculated to obtain the series materials with different concentration of Pd, denoted as: TiO_2, 0.3 wt% Pd/TiO_2, 0.5 wt% Pd/TiO_2, and 1.0 wt% Pd/TiO_2.

In the metal sol method, PVA solution (1 wt%) and solution of $PdCl_2$ were added to an Erlenmeyer flask. The solution was stirred rapidly at low temperature. $NaBH_4$ solution was then dripped slowly into the flask as the mixture was being stirred. Afterward, TiO_2 (P25) was added quickly into the flask and was stirred for another 4 hours. While this process was taking place, the pH value of the mixture was adjusted to less than 5. The mixture must always be cooled by placing it in an ice bath [15,16]. Then, the mixture was filtrated and washed with boiling water. The gray solid obtained after the filtration was dried overnight at 80°C. The solids after the drying are ground to a fine powder. Powder is calcined at 350°C for 2 hours with the presence of the inert gas. The obtained catalyst had a light gray color, with concentration of Pd, denoted as: 0.5 wt% Pd/TiO_2_MS.

The photocatalytic activity for toluene removal of the samples was measured using an annular photocatalytic reactor. To investigate the photocatalytic activities, 0.2 gram of each material was dispersed in 20 ml of C_2H_5OH 99.5 wt% solution and then be coated onto a quartz annular reactor with the diameter and the length to be 20 mm and 250 mm, respectively. After completely coating, the reactor was dried at 80˚C overnight. Before carrying VOCs photocatalytic oxidation, all materials coated on reactor were calcined for 2 hours at 400˚C under ambient pressure. The catalyst-coated glass-tube was set in an annular photocatalytic reactor with four Xe – lamps, symmetrically placed in the reactor (10W per unit, Black light UV, 352nm, Sankyo Denki, Japan). Gas mixtures of toluene, oxygen, and water vapour, and nitrogen was introduced into the annular reactor at fixed flow rate of 50 mL/min in total. The toluene and water vapor in the stream was generated by bubbling method. In addition, before each photocatalytic experiment with light, the feed stream was flowed in the reactor in dark condition for saturating adsorption. After an adsorption equilibrium was reached, UV light was irradiated by the four lamps. The toluene concentrations were analyzed by a Flame Ionization Detector (FID) in a gas chromatography (Hewllet Packard 5890plus) which equipped with a 6-way valve for online injection. In this report, the experiments were conducted to investigate the effects of catalysts, reaction temperature, and reaction time, humidity and toluene concentrations.To investigate the photocatalytic activity ofmaterials for aldehyde VOCs treatment, the toluene in the feed stream above was replaced by formaldehyde (HCHO). The experimental procedure of HCHO was the same with the investigation of toluene. However, only the best activity material was used this experiment, and the

effect of HCHO concentration in feed stream on the photocatalytic activity was also studied.

Crystalline structure of above four catalysts was analysed by powder X-Ray diffraction using Bruker D2 diffractometer, with Cu Kα radiation (λ = 1.54184Å) operated at 30 kV and 10 mA, over a 2θ range from 10° to 80°. Phases of each catalysts were identified by matching experimentally patterns to the JCPDS powder diffraction file. The textual properties of the support GAC and all materials were determined by N2 adsorption at -196°C, with a Nova 2200e machine. Previous to measurements, all of them were out-gassed under vacuum (<10^{-5} Pa) at 300 °C for 1 hour. Specific surface area, $S_{B.E.T.}$ was calculated using B.E.T method. Micropore volume was calculated by application of the Dubinin – Radushkevich (DK) equation. The actual metal content on the catalysts was determined by ICP-OES analysis with an Optima 7300DV spectrometer. The morphology and microstructure of each catalyst and GAC were observed by the scanning electron microscopy (SEM) using Hitachi S-4800 and transmission electron microscopy (TEM) using JEM – 1400, 100 kV.

Results and Discussion

To understand about the textual properties of prepared materials, the specific surface area, $S_{B.E.T}$, was calculated using B.E.T method and ICP-OES analysis was used to determine the Pd contents in all materials, the results were summarized in Table 1. As one can see, by wet impregnation method, when the Pd content increase, the specific surface area (S_{BET})of these materials was decreased because a well-know that the surface areas of Pd metal and Pd oxide were lower than TiO_2. However, in case of material synthesized by sol-gel method, 0.5 wt% Pd/TiO_2, its surface area was seem to be the same with raw TiO_2 because addition species was in form of nano particles, thus its overall $S_{B.E.T}$ was not changed significantly. The actual Pd content of all materials was lower than the nominal Pd content, and these results indicated that some amount of Pd precursor was lost during the wet impregnation process and could incorporate onto TiO_2. However, the efficiency of sol-gel method was better than the normal wet impregnation, about 94% of Pd was incorporated with TiO_2, higher than the normal method about 20%.

Table 1: Properties of the photocatalysts

No.	Sample	$S_{B.E.T}$ (m^2/g)	Pd content (wt%) (ICP)
1	TiO_2	44.0	-
2	0.3 wt% Pd/TiO_2	35.0	0.22
3	0.5 wt% Pd/TiO_2	30.2	0.37
4	1.0 wt% Pd/TiO_2	-	0.74
5	0.5 wt% Pd/TiO_2_MS	43.8	0.47

The XRD patterns of prepared materials were shown in Fig 1 for understanding the crystal structures. In the first pattern representing for raw TiO_2, the characteristic peaks of TiO_2 were detected at 2θ ≈ 25.2 ° (the strongest peak), 36.8°, 48° 53.7°, and 55°. The second pattern representing for material 1.0 wt% Pd/TiO_2 was similar to the first one, however, two characteristic peaks of Pd metal appeared at 2θ ≈ 40.2° and 46.7°, and this was the reason why the shoulder of TiO_2 characteristic peak at 2θ ≈ 48° to be broader than its original peak. No peak was detected for 0.3 wt% Pd/TiO_2 and 0.5 wt% Pd/TiO_2, which may be due to the small content of Pd and its well-dispersion on the TiO_2 surface. In addition, the characteristic peaks of Pd metal in its XRD pattern were less intense even though it is the highest actual Pd content (0.74 wt%), it could be ascribed that Pd metal particles were dispersed finely with small particles size on TiO_2 substrate.

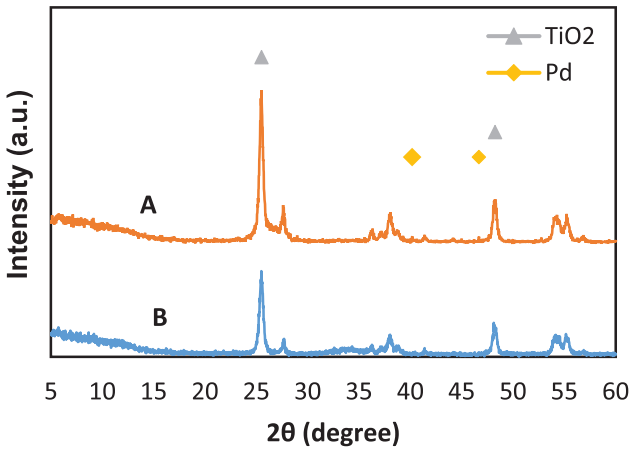


Fig 1. XRD patterns of Pd/TiO_2 (A) and TiO_2 (B)

The distribution of Pd was observed with high resolution scanning electron microscopy (SEM) and showed in Fig 2. With high resolution (x5000), one can see that Pd dispersed finely on the surface of TiO_2 substrate.

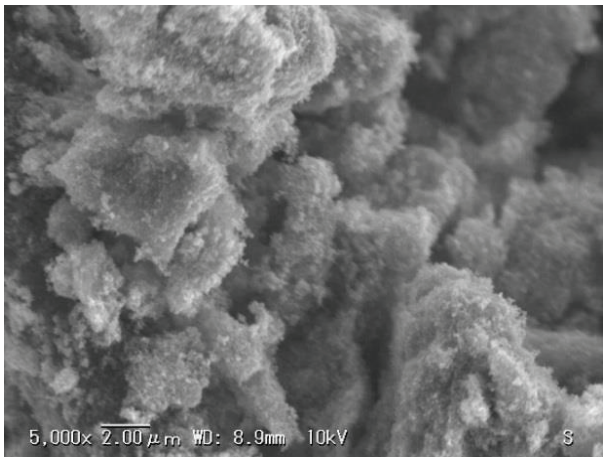


Fig 2. SEM image of 0.5 wt% Pd/TiO_2

The toluene removal efficiencies of two materials raw TiO_2 and 0.3 wt% Pd/ TiO_2 were studied in two continuous separated steps: light-off and under X – lamps. The investigating conditions were the same, Cin = 314 ppm, RH = 60%, F = 3 L/hr, and the total process time was 140 mins. Results were shown in Fig 3. And from the GC-FID peak, there were no abnormal constituents, there were only toluene, thus this photocatalytic reaction did not created by-product, there could be CO_2 and H_2O and untreated toluene in the outlet gas. In the first light-off steps, from 10 mins to 60 mins, the toluene conversion curves of raw TiO_2 and TiO_2 impregnated by Pd were similar. However, as mentioned above, the SB.E.T of material after impregnating was be decreased about 20%, and if under light-off condition, there were toluene adsorption only, the amount of toluene adsorbed on impregnated material should be reduced 20% also. Indeed, from some calculating from equation 1, the adsorption capacity of 0.3 wt% Pd/ TiO_2 was lower than raw TiO_2 about 20%, and after 60 mins of process, the C_{out} of them was nearly the same with C_{in}. It means that in light-off condition, whether raw TiO_2 or TiO_2 with promoter, toluene removal mechanism was adsorption only.

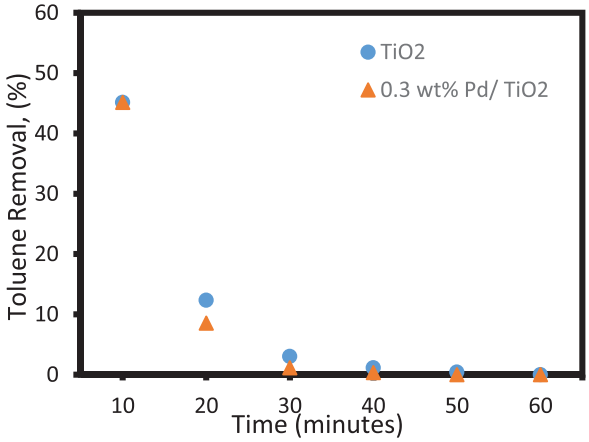


Fig 3. The saturated adsorption time in dark of toluene on TiO2 sample and Pd/TiO_2 sample

WhenX-lamps was turned on, the toluene conversion of these materials was increased magnificently, and especially was higher than the maximum toluene conversion in the adsorption step ($X_{toluene}$ = 50.3% and 65.9% for 0.3 wt% Pd/ TiO_2 and TiO_2, respectively). Results were shown in Fig 4. This results and phenomenon were agreed with literature of photocatalytic oxidation of VOCs by raw TiO_2 and modified TiO_2. With the assist of UV light, the photon energy was equal or exceeded the band gap energy Eg between the valence band (VB) and conduction band (CB), the electron-hole pairs were created in the semiconductor, dissociating into free photoelectrons in the conduction band and photo-holes in the valence band. And in the presence of H_2O molecule, the free hydroxyl radicals OH* were created – a principal and crucial VOCs oxidized agent in almost photocatalytic reaction. In the first 50 mins after light-on, the toluene conversion curves of raw TiO_2 and 0.3 wt% Pd/TiO_2 were similar, however the positive effects on photocatalytic oxidation of toluene exhibited after 60 mins of reaction. In case of TiO_2, the photocatalytic oxidation activity was almost continuous declined, and the deactivation of TiO_2 could be observed after 100 mins under toluene vapor. In contrast with raw TiO_2, the presence of Pd maintained the toluene conversion, around 15%, over the period of reaction time. This phenomenon could be ascribed for Schottky barrier formation between metal-semiconductor interface, since the electrons transferred to the metal particles could favor reduction reactions on their surface and prevent hole-electron recombination.

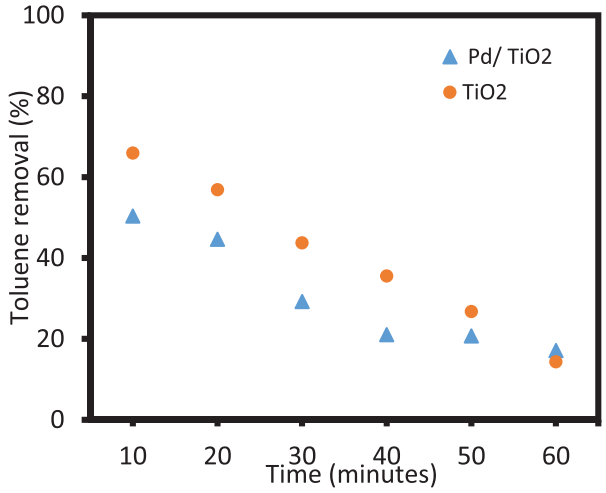


Fig 4. Comparison toluene conversion between TiO_2 and 0.3 wt%Pd/TiO_2

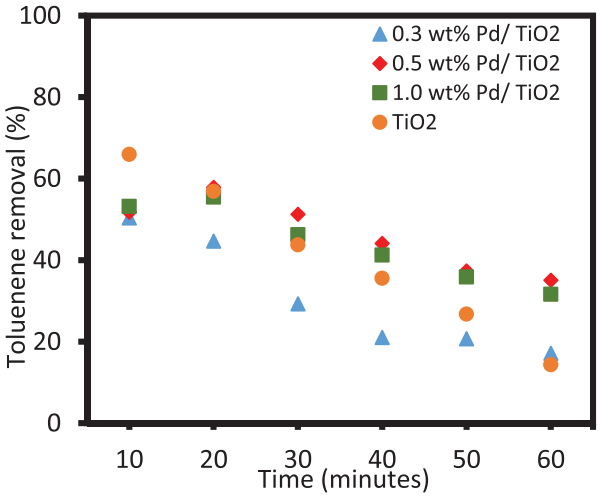


Fig 5. The effect of different amount of additional adsorbent

(Conditions: Flowrate = 3.0 L/h, RH 60%,

mCatalyst = 0.2g, Ctol = 314 ppm, 40°C)

The effects of Pd concentration on the photocatalytic activity of materials Pd/TiO_2 were shown in Fig 5. A series of wet impregnation Pd/TiO_2, 0.5 wt% Pd/TiO_2 and 1.0 wt% Pd/TiO_2 were prepared by the same methods and carried out in the same condition reaction with 0.3 wt% Pd/TiO_2. And in this research, the Pd content was seemed to be not changed the photocatalytic activity of TiO_2 significantly. After light-on, the conversion of three materials was the same, about 53.1%. Even though the trend of their toluene conversion curves was similar, but the equilibrium conversions of 0.5 wt% and 1.0 wt% Pd/ TiO_2 were higher than about 9% that of 0.3 wt% Pd/ TiO_2. Lee et al. also researched about photocatalytic oxidation of Pd/TiO_2 system, they shown that in the presence of PdO, the activity increased because PdO was also oxygen vacancy suppliers, thus it played a co-catalyst role with TiO_2 in VOCs photocatalytic oxidation [14]. Indeed, in this study, when increasing Pd content, especially in case of 1.0 wt% Pd/TiO_2, the initial conversion as well as equilibrium conversion were higher than that of lower Pd content. In addition, in an independent research of Amir Homayoun Keihan et al., they ascribed this phenomenon for the surface plasmon resonance, when metallic Pd content increase, the photocatalytic activity increased.

To investigate the effects of reaction temperature on the photocatalytic activity, material 0.5 wt% Pd/ TiO_2 was used to carry out reaction at 40 ˚C and 80˚C, the results were shown in Fig 6. The toluene conversion increased about 10% as temperature increase 40 ˚C. A well-known theorem Brownian motion that the random motion of molecules increase when temperature of the system increase, lead to collision probability increase also. In this case, the probability of free radical oxidizing agent OH* come in contact with VOCs molecule at 80 ˚C was higher than that at 40 ˚C, thus the conversion was up to 35.8% at equilibrium, and maximum conversion was about 63.2%.

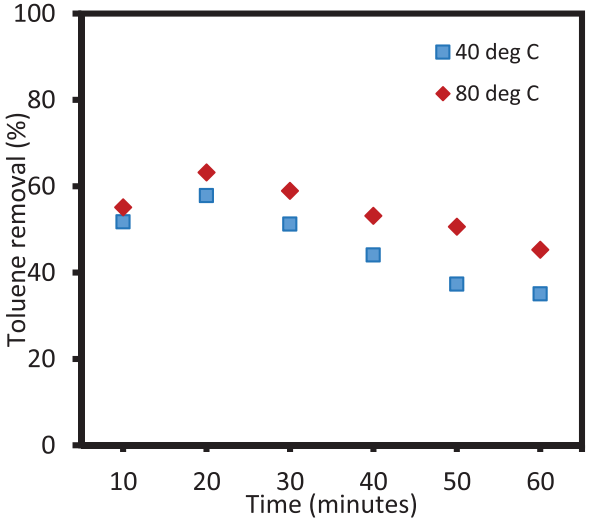


Fig 6. The effect of reaction temperature on 0.5 wt% Pd/TiO_2 sample

The effect of the inlet toluene concentration was investigated on 0.5 wt% Pd/TiO_2 photocatalyst. The results were shown in Fig 7.When the inlet toluene concentration increases from 314 ppm to 832 ppm, the conversion was reduced. If the maximum conversion was 63.2% for C_{in} = 314 ppm, that of C_{in} = 528 ppm and 832 ppm were only 50.6% and 48.7%, respectively. Thesedata could be ascribed for the relative rate of created free radical OH* was lower than the rate of toluene molecule came into

active area of reactor and led to low conversion at high toluene inlet concentration.

With Pd/TiO_2 catalytic system in this work, the activity increases when the humidity increased. Indeed, from the results in Fig 8, using material 0.5 wt% Pd/ TiO_2 at 80°C, the highest conversion was observed at RH = 60%, and the lowest one was being with RH = 15%. As mentioned about the photocatalytic mechanism above, the oxidizing agent is free radical OH* which H_2O vapor is precursor created by photoelectron, thus, if decrease H_2O concentration or reduce RH in the inlet gas, there were not enough relative OH* supplier for photocatalytic reaction, and the result could be low toluene conversion. In this case, when decreasing of 30% in RH, the toluene conversion was reduced about 14%.

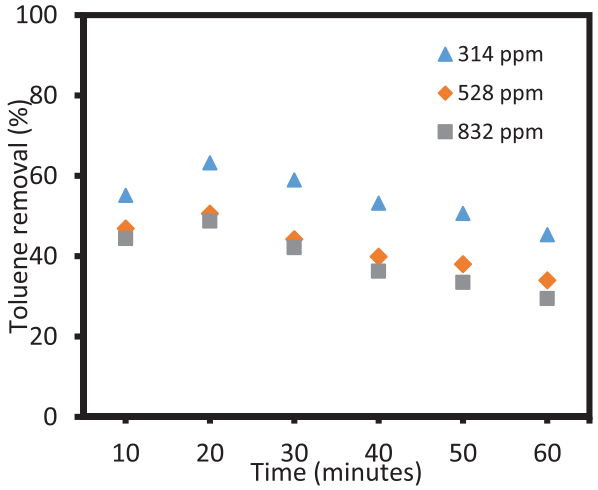


Fig 7. The effect of toluene concentration on activity of 0.5 wt% Pd/TiO_2 photocatalyst

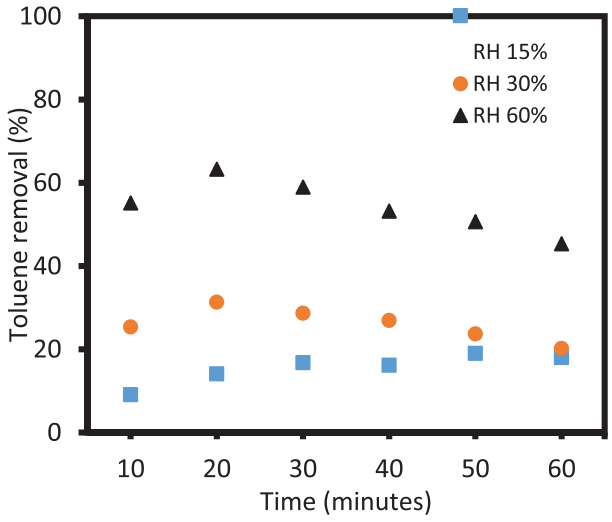


Fig 8. The effect of water content onactivity of 0.5 wt% Pd/TiO_2 photocatalyst

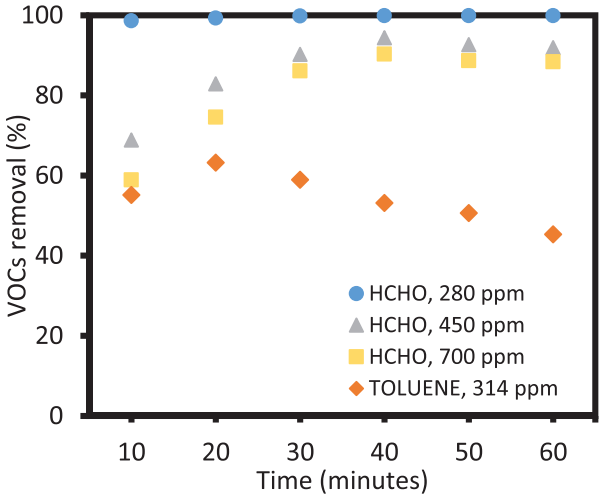


Fig 9. Photocatalytic activities of 0.5 wt% Pd/TiO_2 on different VOCs

This work also expanded photocatalytic ability of material system Pd/TiO_2 for formaldehyde VOC group, and HCHO was chosen for comparation with aromatic VOC group. As one can see in Fig 9, this material removed HCHO absolutely, conversion was 100% in 280 ppm of HCHO and seem to be not change over the reaction time. When the inlet toluene concentration increases from 280 ppm to 700 ppm, the conversion was reduced. If the maximum conversion was 68.83% for C_{in} = 450 ppm, that of C_{in} = 700 ppm was only 58.89%, respectively. This result came from the huge differences between molecule structure of HCHO and toluene, the aromatic structure was more stable than that of formaldehyde, thus free radical OH* attached and cracked HCHO to CO_2 and H_2O easier than toluene.

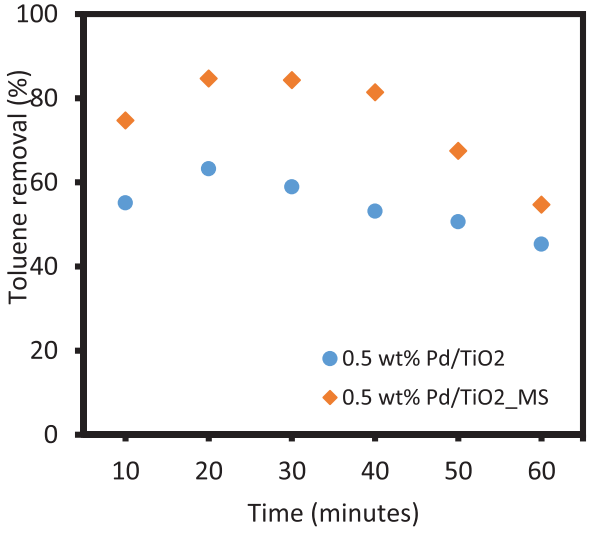


Fig 10. Photocatalytic activities of 0.5 wt% Pd/TiO_2 by different synthesis methods (Wet impregnation and Sol-metal)

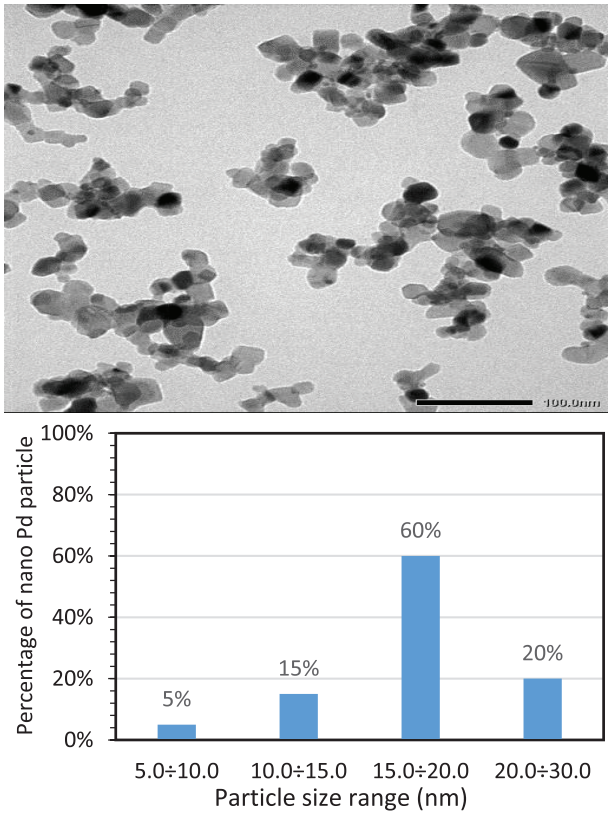


Fig 11. The TEM image of Pd/TiO_2 sample (Metal-sol synthesis method) (top) and Particle Size Distribution (bottom)

Finally, the point of view of this work is created a material that can be used in industrial application, almost materials were synthesized by a simple wet impregnation method. And in comparison with 0.5 wt% Pd/TiO_2 synthesized by an academic method, sol metal, to get the Pd particle in nano size, from 15 nm to 20 nm, the results shown in Fig 11, the photocatalytic conversion was the same with normal 0.5 wt% Pd/TiO_2 over the reaction time of 140 minutes as shown in Fig 10. However, the maximum conversion of sol metal Pd/TiO_2 was higher than that of normal Pd/TiO_2. This is the first paper published this phenomenon. It could be explained that Pd metal in nano size promoted photocatalytic activity of TiO_2 following surface plasmon resonance mechanism. However, over reaction time, the Pd metal nano particles agglomerated to form the large particle size, thus after a period of reaction time, the toluene conversion of Pd/TiO_2 synthesized by either sol metal or normal impregnation method approached to each other.

Conclusions

This study reported the two methods for synthesis of Pd/TiO_2 photocatalystsandtheir application for removal of VOC pollutantsin highly humid condition. The addition of palladium partially stabilized the catalysts against the deactivation induced by the partially oxidized products of the reaction. In the annular photocatalytic reactor with coated 0.5wt.% Pd/TiO_2, the maximum toluene removal efficiencies were 63% by wet impregnation method and 85% by the sol metal synthesis method in the case of the initial toluene concentration 314 ppm and 60% humidity. The process can also be used for HCHO removal in humid condition.

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