

Research Article

Photooxidation of Toluene: Correlation of Noble Metal Loading on Titania and Activation Energy

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A series of platinum and palladium supported on titania catalysts were prepared by wet impregnation method with the Pt or Pd loading varying in the range of 0.1–1.2 weight percent. The catalysts were characterized by SEM, EDX, XRF, XRD, FT-IR, and BET surface area analysis. The catalysts were tested for their efficiency in the liquid phase solvent-free photooxidation of toluene to benzyl alcohol and benzaldehyde in the presence of molecular oxygen. The effect of noble metal contents on the activation energy was studied. Activation energy was found to be in a reciprocal relation to the platinum or palladium content of the catalyst. The percent conversion of toluene was observed to increase in response to an increase in the metal loading on titania. The apparent quantum yield, however, was independent of the platinum or palladium content of the catalyst.

1. Introduction

Photocatalysis is based on the consumption of solar energy and has been extensively considered to be the approach of green chemistry. There are many applications of titanium dioxide such as scratch-resistant optical coating paint pigments, which can also show high activity to photooxidation reaction, in which the researchers are beginning to exploit the field [1]. TiO₂ is a well-known and most applicable photocatalyst; it provides a best agreement between aqueous media and catalytic activity. It has been broadly studied due to its outstanding properties such as thermal stability, nontoxicity, low cost, availability, chemical inertness, and oxidizing ability of organic compounds [2–5]. Below 390 nm, titania can be activated by UV radiations. Absorption of light results in charge production and consequently activity is increased. Photocatalytic reactions of TiO₂ have attracted much attention of the researchers in the field of organic

synthesis [6–8]. The photocatalytic activity of titania depends on its crystalline phase. TiO₂ (anatase) was thoroughly investigated as a photocatalyst for the oxidation of cyclohexane and cyclohexanol. The photocatalytic activity of titania can be enhanced by incorporating metal ions. A variety of methods such as precipitation, doping, and impregnation are used to introduce metal ions into titania [9–11].

Recently, the effects of noble metals such as platinum, gold, palladium, and rhodium on the photocatalytic activity of titania have been extensively studied [12–15]. It has been found that the addition of these noble metals substantially improves the photocatalytic activity of titania. This effect may be attributed to shutting and storing of photogenerated electrons from the titania to acceptor. Platinum loading especially effectuates a remarkable enhancement in the photocatalytic activity of titania through the formation of Schottky barrier at the Pt or Pd/TiO₂ interface [16]. However, many parameters can alter the enhancing effect of noble metal

on the photocatalytic activity of titania such as surface conditions, particle size, noble metal loading, dispersion of active metal on the surface, and the method adopted for deposition of noble metals [17–20].

In this study, our aim was to explore the correlation of noble metals loading such as platinum and palladium on titania and activation energy, in the liquid phase photooxidation of toluene in solvent-free condition with molecular oxygen.

2. Experimental

2.1. General. All chemicals used in this study were of high purity grade and were used without further purification. Mercury arc lamp (TQ-150, 180 W) was used as a light source, while glass filter was used to filter UV radiation. Actinometer (potassium oxalate-ferrioxalate) was used to determine lamp flux. Gases like nitrogen, oxygen, and hydrogen were supplied by BOC Pakistan and were further purified by specific filters (C.R.S.Inc.202268 and C.R.S.Inc.202223).

2.2. Preparation of the Catalyst. TiO_2 was prepared from its precursor compound (TiCl_4) by treatment with ice cold diluted H_2SO_4 solution. The mixture was vigorously stirred for 30 minutes and then heated at 60°C. The mixture was cooled to room temperature for ammonolysis. At pH 7, white precipitate of titania was filtered out from the mixture, washed, dried, and then calcined at 400°C (1°C/min) and retained the temperature for 6 hours.

Platinum or palladium supported on TiO_2 , with metal content ranging from 0.1 to 1.2 wt%, was synthesized by incipient wetness technique. A paste of TiO_2 was formed in the aqueous solution of PtCl_4 or PdCl_2 (containing calculated amount of Pt/Pd) and dried in oven at 105°C overnight. The sample was then subjected to calcination at 400°C (1°C/min) and then maintained for 6 hours at the same temperature. The calcined catalyst was pulverized and finally reduced in a mixture of H_2 and N_2 gases at a flow rate of 40 mL/min for 9 hours at 240°C.

2.3. Characterization of the Catalyst. The platinum and palladium supported on TiO_2 catalysts were characterized by modern technique such as scanning electron microscopy (SEM) of the sample and were recorded on SEM (JSM 5910, Jeol, Japan), energy dispersive X-ray spectroscopy (EDX) of the prepared catalyst was recorded on EDX detector (INC200, Oxford, UK), and X-ray fluorescence spectrometry was performed by XRF, Rigaku ZSX-100e. Metal dispersion was calculated on the basis of CO chemisorption, where $M/\text{CO} = 1$. XRD was performed by X-ray diffractometer (Rigaku D/Max-II, Cu Tube, Japan), and surface area of the catalyst was determined by surface area and pore size analyzer (Quantachrome, Nova 2200). FT-IR spectra of the catalysts were recorded by Fourier Transform Infrared Spectrophotometer “IR Prestige, Shimadzu Japan.”

2.4. Catalytic Test. Pyrex glass batch reactor was loaded with 20 mL toluene and 100 mg catalyst. Nitrogen and oxygen

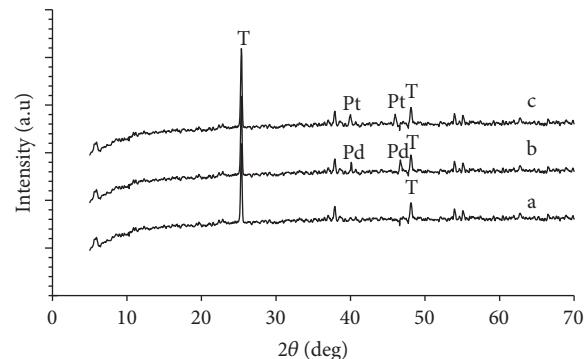


FIGURE 1: XRD pattern of (a) anatase TiO_2 , (b) Pd/TiO_2 , and (c) Pt/TiO_2 (T: anatase TiO_2 , Pt: platinum, and Pd: palladium).

were bubbled through the reaction mixture with their combined flow rate of 40 mL/min while the reaction mixture was irradiated (lamp flux; $1.28 \times 10^{17} \text{ h}\nu/\text{s}$) at a specified temperature (303, 313, 323, and 333 K) for a specified duration (1.5–3 hrs). On completion of the runs, each sample was filtered, treated with excess of water in order to remove the trace of benzoic acid, and analyzed by GC (PerkinElmer Clarus 580) equipped with FID and column (rtx@-Wax 30 m, 0.5 mm ID, and 0.5 nm) for quantification of benzyl alcohol and benzaldehyde. Apparent quantum yield was calculated by using the standard method [21] with the following formula:

$$\Phi_a = \frac{(-d[C_r]/dt)V}{I_i} \Big|_{t=0} \quad (1)$$

where Φ_a is apparent quantum yield, I_i (intensity of incidence irradiant) = $d[\text{hv}]_{\text{incidence}}/dt$, C_r is concentration of reactants, and V is volume of suspension.

3. Results and Discussion

3.1. Characterization of the Catalyst. XRD reflections obtained for titania and metal supported on titania are presented in Figure 1, which shows the characteristic anatase peaks at $2\theta = 25^\circ$ and 48° , and the observed pattern clarifies the absence of brookite and rutile phase of titania. No peaks for platinum or palladium were recorded at low Pt or Pd loading, while the presence of platinum peaks appeared at $2\theta = 40^\circ$ and 46° as platinum loading exceeded 1 wt%, while palladium is indicated by peaks appearing at $2\theta = 40.1^\circ$ and 46.7° [22]. The SEM images of noble metals supported on TiO_2 (ranging from 15 to 110 nm) are presented in Figure 2, which show smooth morphology of the catalyst surface. The EDX spectrum of the Pt or Pd/ TiO_2 is presented in Table 1 which clearly confirms the presence of Pt and TiO_2 or Pd and TiO_2 in its structure; there is no other element or chloride ion present on the surface of titania. BET surface area of TiO_2 was $55.3 \text{ m}^2/\text{g}$ while platinized titania had a surface area of 41.7, 35.6, 31.9, 29, and $26 \text{ m}^2/\text{g}$ for 0.1 wt% Pt/TiO_2 , 0.5 wt% Pt/TiO_2 , 0.7 wt% Pt/TiO_2 , 1.0 wt% Pt/TiO_2 , and 1.2 wt% Pt/TiO_2 , respectively, as shown in Table 2. The decreasing trend of surface area with Pt loading may be attributed to

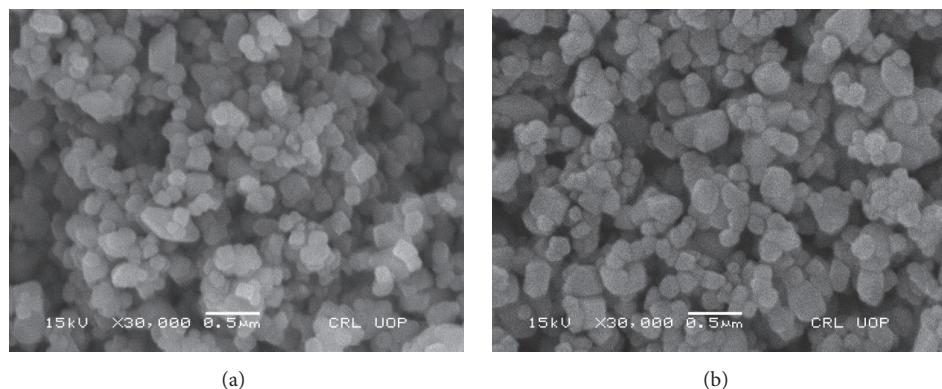
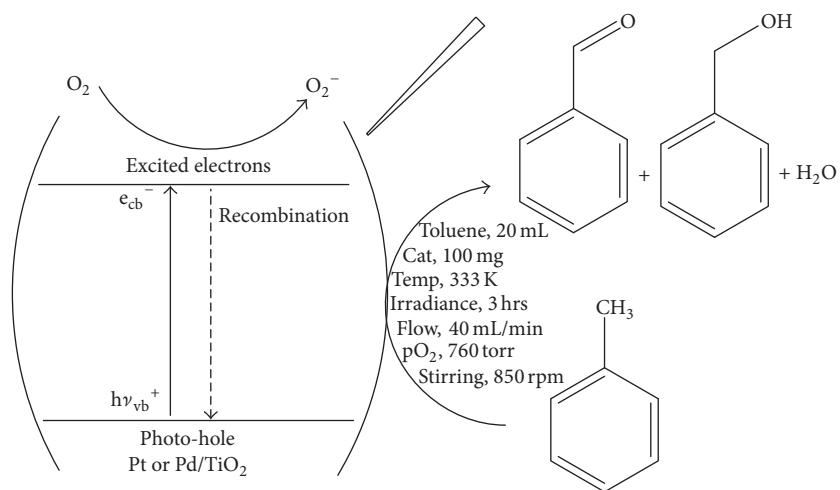


FIGURE 2: SEM images of (a) 0.1% Pt/TiO₂ and (b) 0.1% Pd/TiO₂ used as a photocatalyst for liquid phase oxidation of toluene.



SCHEME 1: Pt/TiO₂ or Pd/TiO₂ catalyzing photooxidation reaction of toluene.

the blockage of surface pore by platinum or perhaps high temperature treatment makes the catalyst aggregated and further reduces the surface area from 0.1 to 1.2 wt% Pt/TiO₂. And the surface area remained almost constant, without showing any change in response to palladium loading in the range of 0.1 wt% to 1.2 wt%. The XRF analysis confirmed that the Pt loading results on TiO₂ were 0.102, 0.51, 0.73, 1.0, and 1.2 wt%, while the results for Pd loading on TiO₂ were 0.112, 0.53, 0.76, 1.25, and 1.32, respectively. The results provided by XRF showed very close agreement with the expected results. From Table 2, it can be seen that the dispersion of platinum on the support decreases from 35.8% to 17.5% at high Pt loading which explains why characteristic peak for platinum appears in the XRD when Pt loading surpasses 1 wt%. Therefore, optimum Pt loading is critical because well dispersion of platinum on TiO₂ surface may improve the electron surface distribution, while very high and uncontrolled Pt loading favors e⁻/h⁺ (electron/hole) recombination which is undesirable.

3.2. Catalytic Test. The catalysts efficiently catalyzed the liquid phase, solvent-free oxidation of toluene to benzyl

TABLE 1: EDX analysis of the catalysts used for photooxidation of toluene.

Catalyst	Elements	Weight %	Atomic %
TiO ₂	O K	46.35	72.12
	Ti K	53.65	27.88
	Total	100	
Pt/TiO ₂	O K	47.82	73.35
	Ti K	51.97	26.63
	Pt M	0.21	0.03
	Total	100	
Pd/TiO ₂	O K	42.67	69.06
	Ti K	57.18	30.91
	Pd K	0.15	0.04
	Total	100	

alcohol and benzaldehyde, under mild reaction conditions, and the mechanisms are presented in Scheme 1. On photon absorption electron of TiO₂ get exited from valence band to conduction band, creating electron-hole pair. Doping

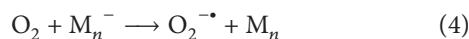
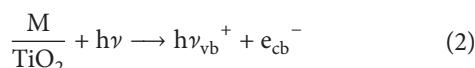
TABLE 2: Surface characteristics of Pt/TiO₂ and Pd/TiO₂ used for the photocatalytic oxidation of toluene.

Catalyst	Surface area (m ² g ⁻¹)	Pt or Pd loading (wt%)		Pt or Pd dispersion (%) [*]
		Expected	Determined	
TiO ₂	55.3	—	—	—
0.1% Pt/TiO ₂	41.7	0.1	0.102	35.8
0.1% Pd/TiO ₂	51.9	0.1	0.112	36.3
0.5% Pt/TiO ₂	35.6	0.5	0.51	30.4
0.5% Pd/TiO ₂	49.5	0.5	0.53	30.9
0.7% Pt/TiO ₂	31.9	0.7	0.73	25.9
0.7% Pd/TiO ₂	47.1	0.7	0.76	25.1
1% Pt/TiO ₂	29.2	1	1.05	22.6
1% Pd/TiO ₂	41.7	1	1.25	21.1
1.2% Pt/TiO ₂	26.4	1.2	1.21	17.5
1.2% Pd/TiO ₂	39.3	1.2	1.32	18.2

* Platinum or palladium dispersion was determined on the basis of chemisorption of platinum or palladium/CO=1.

of metals slows down the electron-hole recombination process and enhanced the photocatalytic activity of the catalyst. Sakthivel and coworkers [23] have reported that up to 1 wt% platinum loading increased the photocatalytic activity of titania while in this study the optimum platinum/palladium loading up to 1.2 wt% was observed. Electrons in the conduction band interact with oxygen while hole in the valence band interacts with toluene and precedes the reaction with free radical chain mechanism.

The platinum and palladium contents on the surface of TiO₂ as a catalyst show enhancing effect on the % conversion of toluene to benzyl alcohol and benzaldehyde in the order 1.2 wt% Pt/TiO₂ > 1 wt% Pt/TiO₂ > 0.7 wt% Pt/TiO₂ > 0.5 wt% Pt/TiO₂ > 0.1 wt% Pt/TiO₂ > TiO₂; similar trend was also observed in Pd/TiO₂ catalyst. However, quantum yield is independent of Pt or Pd loading on TiO₂ as given in Figures 3 and 4. The metals on the surface of titania lead to an increase of the surface barrier and the space charge region becomes narrower, in turn increasing efficiency of the electron-hole separation as presented in Scheme 1:



where M = Pt or Pd which suppressed the recombination process and enhanced the photocatalytic activity of TiO₂ [24]. Furthermore, these metals on the surface of TiO₂ reduce the existence of OH which reduces the photoreactivity [25]. Similarly, the % conversion of toluene to benzyl alcohol and benzaldehyde is too low in dark reaction carried out with 1.2 wt% Pt/TiO₂ or 1.2 wt% Pd/TiO₂ in the same set of reaction conditions. The activation energy was calculated from the temperature study by Arrhenius equation $\ln k = \ln A - (E_a/RT)$ which shows decline as the Pt content of the catalyst increases as shown in Figure 5; 1.2 wt% Pt/TiO₂ has the least activation energy, that is,

47.6 kJmol⁻¹. This is much less than the activation energy of titania which is 60.3 kJmol⁻¹. In the case of Pd/TiO₂ catalyst the correlation activation energy and Pd loading were observed being the same as for Pt/TiO₂ catalyst. Therefore, all proceeding reactions were carried out at 1.2 wt% Pt or Pd/TiO₂. The comparative study of photo and dark oxidation of toluene with 1.2 wt% Pt or Pd supported on TiO₂ showed that the activation energy is too high for dark oxidation of toluene (78.6 kJmol⁻¹ and 80.5 kJmol⁻¹) compared to the photooxidation of toluene (47.6 kJmol⁻¹ and 48.9 kJmol⁻¹), respectively. The % conversion increase as the partial pressure of oxygen was varied in the range of 0–760 Torr till the maximum 4.55 mol% conversion. It was noted that there was no conversion under a flow of nitrogen alone while under a simultaneous flow of oxygen and nitrogen the conversion of toluene to benzyl alcohol and benzaldehyde was observed. The presence of oxygen as an oxidant is thus necessary for oxidation of toluene.

The quantum yield is the highest at intermediate loading (0.5% for Pt and 0.7% for Pd), while the conversion efficiency linearly increases with increase of Pt/Pd loading which may be attributed to catalytic activity of noble metals.

3.3. Blank Test. The reaction was carried out with same reaction conditions, under the standard experimental setup without catalyst loading. The reaction was analyzed for the products (benzyl alcohol and benzaldehyde) but no trace of product was found; therefore, the reaction is photocatalytic oxidation.

3.4. Reusability of the Catalyst. The catalysts were used for six consecutive runs after washing, drying, and treatment at 453 K in inert atmosphere in U shape reactor. The FT-IR spectra of fresh, used, and washed catalysts (Pt/TiO₂ and Pd/TiO₂) were presented in Figures 6 and 7, which revealed that only used catalysts have peaks for (C=O, 1700 cm⁻¹) and broad peak (-OH, 3000–3300 cm⁻¹) while washed catalysts

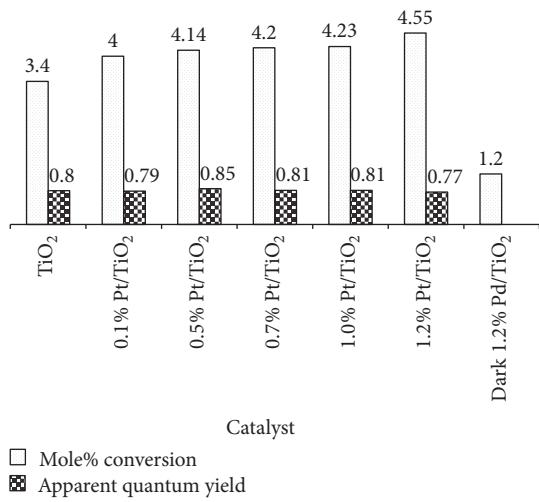


FIGURE 3: Effect of Pt loading on titania used for solvent-free photo/dark oxidation of toluene. *Reaction conditions:* toluene: 20 mL, cat: 100 mg, temp: 333 K, irradiance: 3 hrs, flow: 40 mL/min, pO₂: 760 torr, and stirring: 850 rpm.

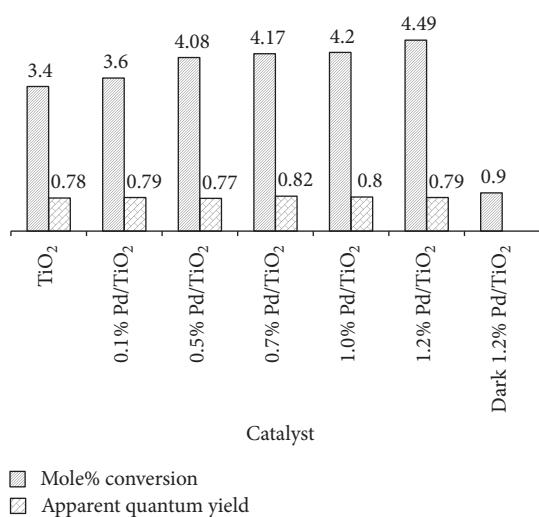


FIGURE 4: Effect of Pd loading on titania used for solvent-free photo/dark oxidation of toluene. *Reaction conditions:* toluene: 20 mL, cat: 100 mg, temp: 333 K, irradiance: 3 hrs, flow: 40 mL/min, pO₂: 760 torr, and stirring: 850 rpm.

have no peaks for coke or residue. The catalysts are quite stable with retaining same catalytic activity for six experimental runs as shown in Figure 8.

4. Conclusion

Pt and Pd supported on titania as photocatalysts are capable of efficiently catalyzing the oxidation of toluene to benzyl alcohol and benzaldehyde in liquid phase solvent-free condition with molecular oxygen. The comparative study of dark and photoreaction reveals that the reaction is photo-dependent. The decrease in activation energy with noble metal loading clarified that up to 1.2 wt% Pt or Pd loading

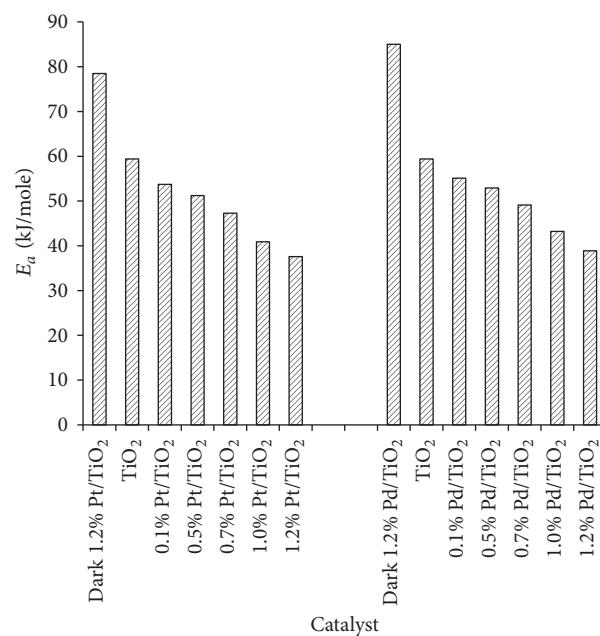


FIGURE 5: Plot for the correlation of activation energy and Pt or Pd content of photocatalyst. *Reaction conditions:* toluene: 20 mL, temp: 303–333 K, cat: 100 mg, irradiance: 3 hrs, flow: 40 mL/min, pO₂: 760 torr, and stirring: 850 rpm.

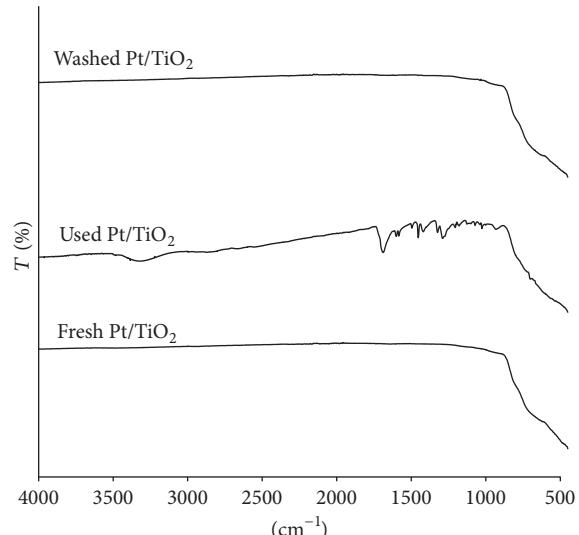


FIGURE 6: FT-IR spectra of fresh Pt/TiO₂, used Pt/TiO₂, and washed Pt/TiO₂.

improved the photocatalytic activity of the catalyst by retarding the electron-hole recombination process. Furthermore, the activation energy shows reciprocal relation to platinum or palladium loading on titania.

Competing Interests

The authors declare no conflict of interests.

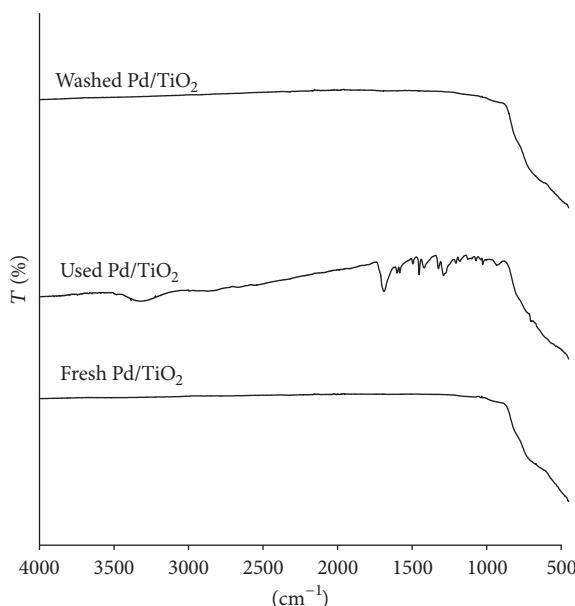


FIGURE 7: FT-IR spectra of fresh Pd/TiO_2 , used Pd/TiO_2 , and washed Pd/TiO_2 .

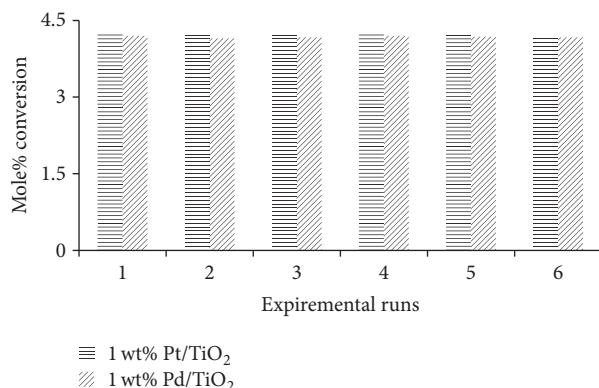


FIGURE 8: Life span of the catalysts for photooxidation of toluene. *Reaction conditions:* toluene: 20 mL, cat: 100 mg, temp: 333 K, irradiance: 3 hrs, flow: 40 mL/min, pO_2 : 760 torr, and stirring: 850 rpm.

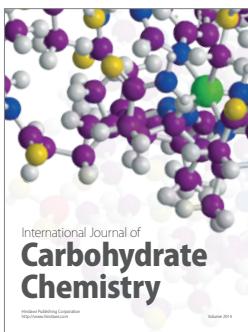
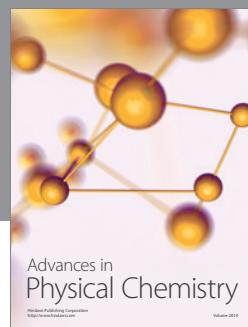
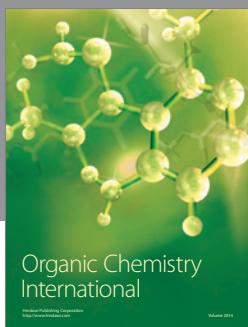
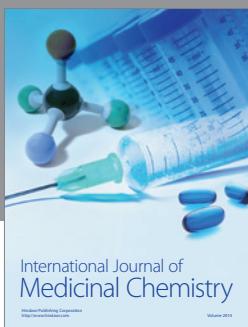
Acknowledgments

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