Photocatalytic Reduction of Nitro Compounds Using TiO_2 Photocatalyst by UV and Vis Dye-sensitized Systems

Chen, Shifu*(陈士夫) Zhang, Huaye(张华烨) Yu, Xiaoling(余晓玲) Liu, Wei(刘伟)

Department of Chemistry, Huaibei Normal University, Huaibei, Anhui 235000, China

Nitro-aromatic compounds can be photocatalytically reduced into the corresponding amine-aromatic compounds using TiO_2 as a photocatalyst in the UV/TiO_2/holes scavenger and Vis/TiO_2/dye-sensitized systems. In the UV/TiO_2/holes scavenger system, reaction substrate alcohols such as methanol could be used as the holes scavengers, and in the Vis/TiO_2/dye-sensitized system, substrate alcohols could be oxidized to the corresponding aldehydes with high selectivity. When methanol was used as the holes scavengers and the illumination time was 6 h, 87.2% of *p*-nitrotoluene could be photocatalytically reduced into *p*-toluidine. In the Vis/TiO_2/dye-sensitized system, the effect of aromatic alcohols for the photocatalytic reduction of nitrobenzene was better than that of other alcohols. At the same time, aromatic alcohols can be easily oxidized, and the production efficiencies of the corresponding aldehydes were higher than those of other alcohols. The possible reaction mechanisms were also proposed.

Keywords photochemistry, synthetic, method, nitro-aromatic compounds, UV/TiO_2/holes scavenger, Vis/TiO_2/dye-sensitized systems

Introduction

Semiconductor photocatalysis has attracted much research attention in the past decades owing to their application in environmental purification, water splitting, and conversion of solar energy into electrical energy, *etc*.[1-6] It is known that when the surface of semiconductor absorbs photons and its energy is equal to or higher than that of the band gap, the low-energy electron of valence band is excited to conduction band, and electron-hole pairs will be produced on the surface of semiconductor. Photo-excited electron has a higher reducing power, and photo-excited hole has a higher oxidizing power. If these photo-excited electron-hole pairs do not recombine, they would have the reactions of reduction and oxidation, respectively.[7-9] The photoinduced reduction of nitrobenzene should attract considerable interest in view of pursuing environmentally ‘benign’ or ‘green’ synthesis, since it consumes low-energy photons and occurs under atmospheric pressure and at room temperature. Therefore, the study on photocatalytic reduction by semiconductor has great significance. Ferry *et al*.[10] and Flores *et al*.[11] have reported the results of photocatalytic reduction of aromatic nitro-compounds in the presence of sacrificial electron donors, respectively. We have reported the results of photocatalytic reduction of nitrobenzene to aniline using titanium dioxide powder as photocatalyst, under the protection of nitrogen and in the presence of holes scavenger, such as methanol, ethanol.[12]

Recently, Zhao and co-workers[4] reported that the selective oxidation of alcohols was achieved under visible-light irradiation in a system containing dye-sensitized TiO_2 and nitroxyl radicals (such as 2,2,6,6-tetramethylpiperidinyloxyl, TEMPO). In the dye-sensitized system, the dye, rather than the TiO_2 catalyst, absorbs visible light and is excited. The process involves two important steps of electron transfer: (1) the electron injection from the excited dye molecule to the conduction band of TiO_2 generating dye radical; and (2) the dye-radical promoted oxidation of TEMPO to $TEMPO^+$, which can selectively oxidize the alcohols to aldehydes. Dioxygen reacts with e_{cb}^- to form O_2^- (which reacts further to give H_2O_2) and enables the excited state of the dye molecules to inject electrons into the conduction band of TiO_2 incessantly. In the system, only when electrons are captured by dissolved oxygen in the solution, can the reaction of selective oxidation of alcohols proceed. The above result really enlightened us. If dissolved oxygen is absent and nitro compounds are added into the reaction system, the selective oxidation of alcohols and photocatalytic reduction of nitro compounds will be achieved under visible-light irradiation in a system containing dye-sensitized TiO_2. At the same time, dye radicals were stable as O_2^-, and H_2O_2 were not formed in the system.

In this paper, we first study the photocatalytic reduction of aromatic nitro-compounds to amine-aromatic compounds using TiO_2 as a photocatalyst under

---

* E-mail: chshifu@chnu.edu.cn; Tel.: 0086-0561-3806611; Fax: 0086-0561-3803141

Received May 3, 2010; revised September 26, 2010; accepted November 22, 2010.

Project supported by the National Natural Science Foundation of China (Nos. 20673042, 20973071) and the Key Project of Science and Technology Research of Ministry of Education of China (208062).

UV-light irradiation. Then, the feasibility of selective oxidation of alcohols and photocatalytic reduction of aromatic nitro-compounds under visible-light irradiation in a system containing dye-sensitized TiO_2 was investigated. And the reaction mechanisms were also studied.

Experimental

Materials

Nitrobenzene, aniline, *p*-nitrotoluene, *m*-nitrotoluene, *o*-nitrotoluene, *p*-toluidine, *m*-toluidine, *o*-toluidine and the anthraquinone dye Alizarin Red (AR) were purchased from Shanghai Chemical Reagent Ltd. TiO_2 powder used in the experiments was prepared by thermal decomposition and calcination of a colloidal solution made by hydrolysis of titanium tetraisopropoxide $[Ti(\textit{iso}\text{-}OC_3H_7)_4]$ in our laboratory. From the analysis, it is known that the TiO_2 sample contains mainly anatase with the mean grain size of 30 nm. Aromatic alcohols, aliphatic alcohols such as benzenemethanol, *p*-methyl benzyl alcohol, propenol, heptanol, butanol, methanol (MeOH), ethanol (EtOH) and other chemicals used in the experiments were purchased from other Chinese chemical reagent company without further purification. They are of analytically pure grade. Deionized and doubly distilled water was used throughout this study.

Photoreaction apparatus and procedure

The experiments were carried out in a photoreaction apparatus. The photoreaction apparatus consists of two parts.[12,13] The first part is an annular quartz tube. A 375 W medium pressure mercury lamp (Institute of Electric Light Source, Beijing) with a maximum emission at about 365 nm and a 500 W Xenon lamp (Institute of Electric Light Source, Beijing) with a maximum emission at about 470 nm, were used as UV and visible light sources, respectively. The wavelength of the visible light is controlled through a cutoff filter ($\lambda > 420$ nm, Instrument Company of Nantong, China). The lamp is laid in an empty chamber of the annular tube, and running water passes through an inner thimble of the annular tube. Owing to continuous cooling, the temperature of the reaction solution is maintained at approximately 30 ℃. The second part is a sealed beaker of 10 cm diameter. At the beginning of the experiment, the reaction solution (UV/TiO_2/holes scavenger system and Vis/TiO_2/dye-sensitized system, volumes are 300 and 100 mL, respectively) containing reactants and photocatalyst was put in the sealed beakers, and a magnetic stirring device was used to stir the reaction solution. The distance between the light source and the surface of the reaction solution is 11 cm. Nitrogen was passed through the solution for 0.5 h before illumination to remove the dissolved oxygen in the reaction solution. In order to disperse the photocatalyst powder, the suspensions were ultrasonically vibrated for 20 min prior to irradiation. After illumination, the samples were taken from the reaction suspension, centrifuged at 7000 r/min for 20 min and filtered through a 0.2 μm millipore filter to remove the particles. The filtrate was then analyzed. For the purpose of determining the reproducibility of the results, at least duplicated actions were carried out under each condition to seek average results.

Analysis

The main products for photocatalytic reduction of aromatic nitro-compounds are aromatic amino-compounds. The products for selective oxidation of alcohols are aldehydes. The production efficiency of aromatic amino-compounds or aldehydes and the residual efficiency of aromatic nitro-compound or alcohol for each sample were calculated from the following formulas:

$$\eta_1 = P_t / C_0 \times 100\% \tag{1}$$

$$\eta_2 = R_t / C_0 \times 100\% \tag{2}$$

where η_1 is the production efficiency of aromatic amino-compound or aldehyde; η_2 is the residual efficiency of aromatic nitro-compound or alcohol; P_t is the amount of aromatic amino-compound or aldehyde in solution after illumination for t; R_t is the amount of aromatic nitro-compound or alcohol in solution after illumination time t; C_0 is the total amount of aromatic nitro-compound or alcohol in solution before illumination.

Alcohols and aldehydes in the solutions were analyzed with a SCHIMADU GCMS-QP2010 Plus. The structures of the products were confirmed by GC-MS comparison with standard samples. Aromatic nitro-compounds concentrations were also determined by gas-chromatography with hydrogen flame detector (SCHIMADU GCMS-QP2010). (GC conditions: chromatographic column: AC20; carrier gas: N_2; flow rate: 30 mL/min; sample injection volume: 4 μL). Amino-compound concentrations in the solutions were determined spectrophotometrically using naphthalene ethylenediamine azo as a developer.

Results and discussion

UV/TiO_2/holes scavenger system

The fixed amount of TiO_2 was 4.0 $g \cdot L^{-1}$, methanol was chosen as holes scavenger. Initial pH of reaction solution is 4.0 and initial concentration of aromatic nitro-compounds was 7.3×10^{-4} $mol \cdot L^{-1}$. The relationships among the residual efficiency of aromatic nitro-compounds, the production efficiency of aromatic amino-compounds and the illumination time were investigated. The results are shown in Figures 1 and 2.

From Figures 1 and 2, it can be seen that the production efficiency of aromatic amino-compounds increases and the residual efficiency of *p*, *m*, *o*-nitrotoluene decreases with the increase of the illumination time. When the illumination time increases from 1 to 6 h, the production efficiency of *p*-toluidine increases from 27.2%

to 87.2%, and the residual efficiency of *p*-nitrotoluene decreases from 46.1% to 1.39%. For *m*-toluidine, the production efficiency increases from 17.5% to 72.7%, and the residual efficiency of *m*-nitrotoluene decreases from 60.5% to 10.5%. For *o*-toluidine, the production efficiency increases from 14.5% to 67.7%, and the residual efficiency of *o*-nitrotoluene decreases from 69.5% to 15.5%. It is clear that the production efficiency of aromatic amino-compound and the residual efficiency of aromatic nitro-compounds are greatly related to the structure of nitro-aromatic compounds. The degree for photocatalytic reduction of aromatic nitro-compounds is as follows: (*p*-nitrotoluene) > (*m*-nitrotoluene) > (*o*-nitrotoluene).

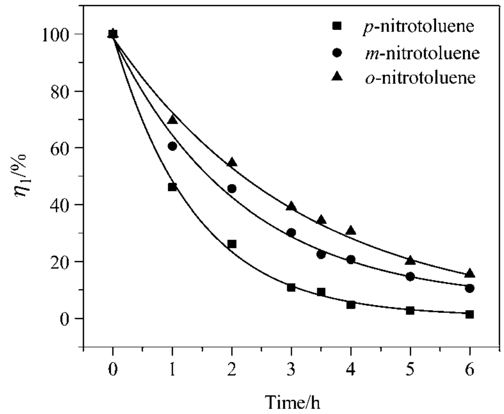


Figure 1 Relationship between the residual efficiency of aromatic nitro-compounds and the illumination time.

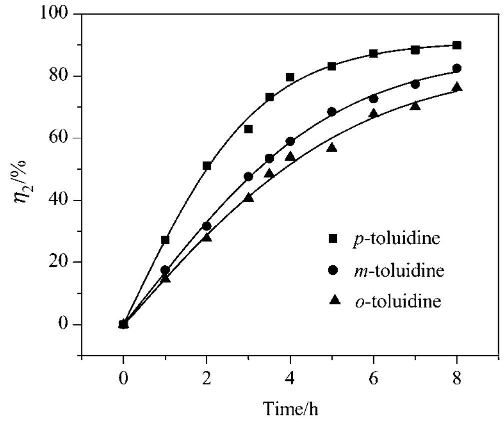


Figure 2 Relationship between the production efficiency of aromatic amino-compounds and the illumination time.

Theoretically, if aromatic nitro-compounds are photocatalytically reduced completely without by-products, 1 mol of aromatic nitro-compounds can produce 1 mol aromatic amino-compounds. From Figure 1 and Figure 2, it is clear that, when the illumination time is 8 h, aromatic nitro-compounds such as *p*-nitrotoluene can not be photocatalytically reduced to amino-compound completely, and it produced 10% or more by-products.

It has been reported that the photocatalytic reduction kinetics for all substrates are found to obey Langmuir-Hinshelwood kinetics model.[11,12] The kinetic curves obtained in the solvent are characteristic for the formal first-order kinetics, and are fitted to the exponential function:

$$C = A + B\exp(-kt) \tag{3}$$

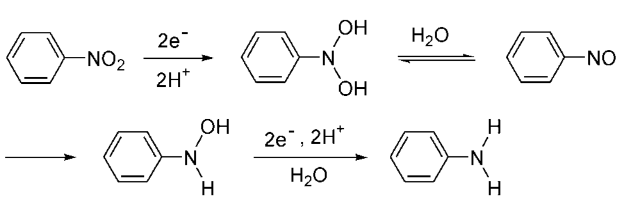
where *t* is illumination time; *C* is the concentration of *p*, *m*, *o*-toluidine or *p*, *m*, *o*-nitrotoluene; *k* is the rate constant of the decrease of aromatic nitro-compounds or the production of amine-aromatic compounds; *A* and *B* are constants. C_t is concentration at the time of *t*.

According to the relationship between the concentration of aromatic nitro-compounds or aromatic amine-compounds and the illumination time, the kinetics equations for photocatalytic reduction of *p*, *m*, *o*-nitrotoluene in methanol are $C_t = 7.3\times10^{-4}/\exp(0.7121t)$, $C_t = 7.3\times10^{-4}/\exp(0.3850t)$ and $C_t = 7.3\times10^{-4}/\exp(0.3211t)$, respectively.

The kinetics equations for the formation of *p*, *m*, *o*-toluidine in methanol are $C_t = -8.01\times10^{-4}[\exp(-0.2934t)-1]$, $C_t = -8.01\times10^{-4}[\exp(-0.1998t)-1]$ and $C_t = -8.01\times10^{-4}[\exp(-0.1735t)-1]$, respectively.

It is believed that the photocatalytic reduction reaction of aromatic nitro-compounds occurs on the surface of TiO_2.[14,15] Under UV illumination, electron-hole pairs are created on the surface of TiO_2. Holes scavengers such as methanol adsorbed on the surface of TiO_2 prevent the recombination of electron-hole pairs by trapping holes, and the photoexcited electrons are strong enough to reduce aromatic nitro-compounds adsorbed on the surface of TiO_2 to aromatic amino-compounds.[11,12,14] In the process, the alcohols as holes scavengers were oxidized to the corresponding aldehydes followed by the mineralization of aldehydes into CO_2 and H_2O.[10,11,16,17]

It was proposed that the photocatalytic reduction of nitro-aromatic compounds was a 6-electron reaction.[12,14,15] The process of photocatalytic reduction of nitrobenzene is as follows: $RNO_2 \rightarrow RNO \rightarrow RNHOH \rightarrow RNH_2$.



In the process, the main intermediates of the photoreduction of nitrobenzene (*i.e.*, nitrosobenzene and *N*-hydroxylaniline) have been detected in our laboratory. It can be seen that the reduction efficiency is influenced by a series of processes and factors including the electron transfer from the conduction band of TiO_2 to a nitro compound, the back-electron transfer from a nitro radical anion to the valence band, and proton availability.[12,15]

Based on the above results, if nitrobenzene is chosen as the deputy, the possible schematic diagram of photocatalytic reduction of aromatic nitro-compounds in the UV/TiO_2/holes scavenger system is proposed in Figure 3.

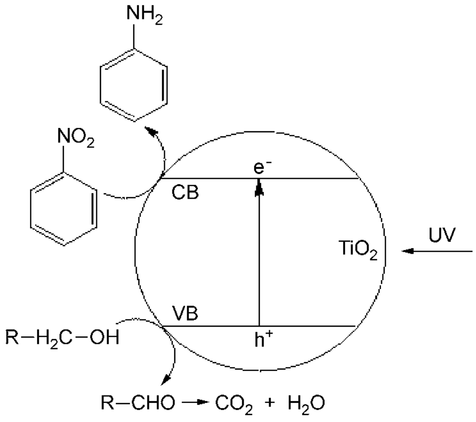


Figure 3 Schematic diagram of photocatalytic reduction of nitrobenzene in the UV/TiO_2/holes scavenger system.

Vis/TiO_2/dye-sensitized system

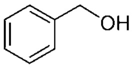
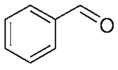
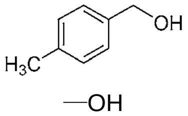
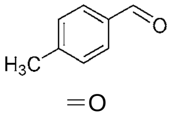
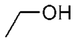
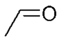
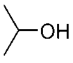
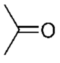
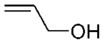
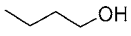
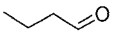
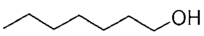
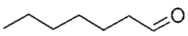
In this paper, we used the commercial anthraquinone dye Alizarin Red (AR) as the sensitizer. It is known that AR has a high extinction coefficient ($\varepsilon_{max}=28000$) at wavelengths of 400—500 nm in the visible region and a redox potential, which is suitable for effectively driving the corresponding events of electron transfer from the excited state of AR to the conduction band of TiO_2. The redox potential $E^0_{AR*/AR+•}$ (−1.57 V vs. standard hydrogen electrode, SHE) is lower than E_{cb} of TiO_2 (−0.50 V vs. SHE).[4,18,19]

The photocatalytic reactions were carried out at five different experimental conditions: (1) AR/TiO_2+O_2, (2) AR/TiO_2+O_2+Vis, (3) AR/TiO_2+N_2, (4) TiO_2+N_2+Vis, (5) AR/TiO_2+N_2+Vis. The results showed that there were no obvious reactions for the photocatalytic reduction of aromatic nitro-compounds and selective oxidation of alcohols under conditions 1, 3 and 4. The selective oxidation of alcohols may be achieved under condition 2, but the photocatalytic reduction of aromatic nitro-compounds did not take place. Only when TiO_2, dye, nitrogen and visible-light irradiation are present, can the photocatalytic reduction of aromatic nitro-compounds and selective oxidation of alcohols occur.

In order to evaluate the photocatalytic reduction of aromatic nitro-compounds and selective oxidation of alcohols, latent solvent carbon tetrachloride and chloroform were chosen as reaction solvents, and nitrobenzene was chosen as a deputy of aromatic nitro-compounds. Reaction condition is as follows: the volume of the alcohol is 5.0 mL; the amount of TiO_2 is 0.4 g; the concentration of nitrobenzene is 0.0406 mol•L^{-1}, and the concentration of AR used is 5.6×10^{-4} mol•L^{-1}. The results are shown in Table 1.

From Table 1, it can be seen that, for the photocatalytic reduction of nitrobenzene, aromatic alcohols and aliphatic alcohols of short chain are better substrates. When benzenemethanol and *p*-methyl benzyl alcohol were used as substrates, the production efficiency of aniline is the highest. When aliphatic alcohols were used as substrates, it is plausible that the aliphatic alcohols of short chain are better than those of long chain. However, the production efficiency of aniline is not correlative with the chain length of aliphatic alcohols. It was reported that when reaction substrate has lower viscosity, higher polarity, lower polarisability and higher rate of polarity/polarisability, it is favorable for the photocatalytic reduction of aromatic nitro-compounds.[20] From Table 1, it is clear that, the easier alcohol is oxidized, the more likely nitro-compounds are

Table 1 Results of the photocatalytic reduction of nitrobenzene and selective oxidation of alcohols[a]

Entry	Substrate	Product	*t*/h	Production efficiency of aldehyde		Aniline/(mol•L^{-1})	
				A	B	A	B
1			18	85.2	85.1	2.52×10^{-4}	2.76×10^{-4}
2			18	80.1	80.6	2.26×10^{-4}	2.36×10^{-4}
3	—OH	=O	18	55.7	58.0	1.41×10^{-4}	1.88×10^{-4}
4			20	52.1	50.5	3.83×10^{-5}	3.85×10^{-5}
5			19	47.9	47.4	4.02×10^{-5}	4.10×10^{-5}
6			30	70.4	71.0	2.89×10^{-4}	3.05×10^{-4}
7			30	47.4	46.3	6.92×10^{-5}	8.92×10^{-5}
8			31	44.6	44.7	9.86×10^{-5}	1.03×10^{-4}

[a] A: Carbon tetrachloride as solvent, B: Chloroform as solvent.

reduced. This may be attributed to the fact, the easier alcohol is oxidized, the more favorable it is for the electron transfer between dye and photocatalyst, which results in the increase of the production efficiency of aniline.

From Table 1, it can be seen that for the selective oxidation of alcohols, the aromatic alcohols substrates such as benzenemethanol and *p*-methyl benzyl alcohol are easily oxidized, and the production efficiencies of the corresponding aldehydes are higher than those of other alcohols. However, aliphatic alcohols exhibited relatively low activity, and with the increase in chain length, the activity decreases gradually. Aromatic alcohol is oxidized more easily than aliphatic alcohol. The reason is that although both of them contain OH group in their structure, the hydrocarbyls connected to OH group are different. The phenyl in the hydrocarbyl of aromatic alcohol is a powerful electrophilic group, and is able to induce α-H on carbon atoms connected to OH group to activate, and causes aromatic alcohol to be oxidized more easily. However, the hydrocarbyl in aliphatic alcohol does not have the ability to activate α-H. The aliphatic alcohol with short chain is easier to be oxidized than that with long chain. The reason is that, the longer the carbon chain is, the stronger electron donating group it will be, which causes α-H to be less activated.

It is interesting that propenol can be oxidized to the corresponding unsaturated aldehyde. The results correspond with the previous report.[4] At the same time, the results also showed that the selectivity of the oxidation of alcohols was high, and all of them exceeded 96%. From Table 1, it can also be seen that the latent solvents have no obvious effect on the photocatalytic reduction of nitrobenzene and selective oxidation of alcohols in the Vis/TiO_2/dye-sensitized system.

The photocatalytic reduction of other aromatic nitro-compounds, such as *p*-nitrotoluene, *m*-nirotoluene and *o*-nirotoluene were also investigated. The result showed that when methanol was used as a reaction substrate and the illumination time was 20 h, the production concentrations of corresponding amino-compounds for *p*-nitrotoluene, *m*-nitrotoluene and *o*-nirotoluene were 2.38×10^{-4}, 1.92×10^{-4} and 1.87×10^{-4} $mol\bullet L^{-1}$, respectively. From the above results, compared with the selective oxidation of alcohols, it is clear that, the efficiency of the photocatalytic reduction of aromatic nitro-compounds is lower. This may be attributed to low efficiency of the electron injection from the excited dye molecule to the conduction band of TiO_2 and the electron transfer from the conduction band of TiO_2 to a nitro compound and proton availability.

It is known that, in the dye-sensitized system, the dye, rather than the TiO_2 photocatalyst, absorbs visible light and is excited.[4] The photoexcited electron injection from the excited dye molecule to the conduction band of TiO_2 generates dye radical. The dye radical can selectively oxidize the alcohols to aldehydes, and it was reduced to dye. The above process achieves the cycle of dye and the dye radical. The photoexcited electrons are strong enough to reduce aromatic nitro-compounds adsorbed on the surface of TiO_2 to aromatic amino-compounds. At the same time, it enables the excited state of the dye molecules to inject electrons into the conduction band of TiO_2 incessantly.

Based on the above results, a possible mechanism is proposed in Figure 4.

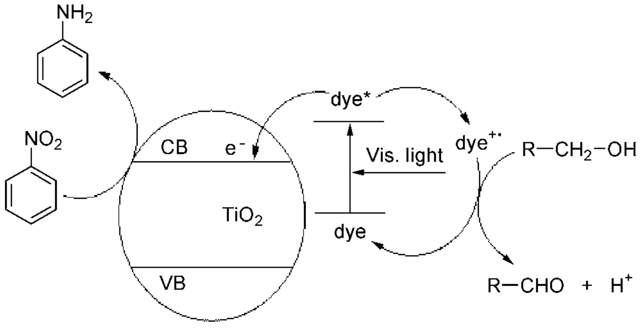


Figure 4 Possible mechanisms of photocatalytic reduction of nitrobenzene in the Vis/TiO_2/dye-sensitized system.

It was reported[21-23] that in the dye/TiO_2-photosensitized reaction, the dye radicals were transient, active species decomposed to small molecules and even further to CO_2 by complicated dioxygen-involved reactions. In the dye/TiO_2-photosensitized system, TEMPO is necessary to maintain the stability of dye radicals and high selectivity.[4] However, in the Vis/TiO_2/dye-sensitized system, because there was no dissolved oxygen in the system and aromatic nitro-compounds acted as electrons scavenger, the dye radicals were stable in the reaction process. The conclusion was verified in our laboratory because in the reaction process, no fragments of dye degradation were found in the chromatographic analysis.

Conclusions

In UV/TiO_2/holes scavenger system, photocatalytic reduction of nitro-aromatic compounds to amine-aromatic compounds can be processed in the presence of sacrificial electron donor such as methanol. When illuminated for 6 h, 7.3×10^{-4} $mol\bullet L^{-1}$ of *p*-nitrotoluene can be photocatalytically reduced completely, and more than 87.2% of *p*-nitrotoluene can form *p*-toluidine in methanol. In Vis/TiO_2/dye-sensitized system, the substrate alcohols could be oxidized to the corresponding aldehydes with high selectivity, and nitro-aromatic compounds could be photocatalytically reduced into the corresponding amine-aromatic compounds. Although the efficiency of photoreduction is low in the system, it achieves double purpose for the selective oxidation of alcohols and the photocatalytic reduction of nitro-aromatic compounds.

References

1 Duncan, W. R.; Stier, W. M.; Prezhdo, O. V. *J. Am. Chem. Soc.* **2005**, *127*, 7941.

2 Lin, J.; Zhu, Y. F. *Inorg. Chem.* **2007**, *46*, 8373.

3 Xue, H.; Li, Z. H.; Dong, H.; Wu, L.; Wang, X. X.; Fu, X. Z. *Cryst. Growth. Des.* **2008**, *8*, 4469.

4 Zhang, M.; Chen, C. C.; Ma, W. H.; Zhao, J. C. *Angew. Chem.* **2008**, *120*, 9876.

5 Liu, S. W.; Yu, J. G.; Stephen, M. J. *Phys. Chem. C* **2009**, *113*, 10712.

6 Yu, J. G.; Yu, X. X.; Huang, B. B.; Zhang, X. Y.; Dai, Y. *Cryst. Growth. Des.* **2009**, *9*, 1474.

7 Claire, C. C.; Delphine, S.; Isabelle, L.; Laurent, R. *Appl. Catal. B*: *Environ.* **2008**, *84*, 835.

8 Li, Z. H.; Dong, H.; Zhang, Y. F.; Dong, T. T.; Wang, X. X.; Li, J. Q.; Fu, X. Z. *J. Phys. Chem. C* **2008**, *112*, 16046.

9 Yu, J. G.; Fan, F. R. F.; Pan, S. L.; Lynch, V. M.; Omer, K. M.; Bard, A. J. *J. Am. Chem. Soc.* **2008**, *130*, 7196.

10 Ferry, J. L.; Glaze, W. H. *Langmuir* **1998**, *14*, 3551.

11 Flores, S. O.; Rios-Bernij, O.; Valenzuela, M. A.; Córdova, I.; Gómez, R.; Gutie′rrez, R. *Top. Catal.* **2007**, *44*, 507.

12 Chen, S. F.; Zhang, H. Y.; Yu, X. L.; Liu, W. *Chin. J. Chem.* **2010**, *28*, 21.

13 Chen, S. F.; Zhao, W.; Liu, W.; Zhang, H. Y.; Yu, X. L. *Chem. Eng. J.* **2009**, *155*, 466.

14 Kamat, P. V. *Chem. Rev.* **1993**, *93*, 267.

15 Fox, M. A.; Dulay, M. T. *Chem. Rev.* **1993**, *93*, 341.

16 Thuan, D. B.; Akira, K.; Shigeru, L.; Michio, M. *J. Am. Chem. Soc.* **2010**, *132*, 8453.

17 Ouidri, S.; Khalaf, H. J. *Photochem. Photobiol. A*: *Chem.* **2009**, *207*, 268.

18 Garcia, J. C.; Takashima, K. J. *Photochem. Photobiol. A*: *Chem.* **2003**, *155*, 215.

19 Liu, G. M.; Li, X. Z.; Zhao, J. C.; Horikoshi, S.; Hidaka, H. *J. Mol. Catal. A* **2000**, *153*, 221.

20 Cecchetto, A.; Fontana, F.; Minisci, F.; Recupero, F. *Tetrahedron Lett.* **2001**, *42*, 6651.

21 Brezova, V.; Blazkova, A.; Surina, I.; Havlinova, B. *J. Photochem. Photobiol. A*: *Chem.* **1997**, *107*, 233.

22 Sheldon, R. A.; Arends, I. W. C. E. *Adv. Synth. Catal.* **2004**, *346*, 1051.

23 Recupero, F.; Punta, C. *Chem. Rev.* **2007**, *107*, 3800.

(E1005031 Zhao, C.; Fan, Y.)