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Photocatalytic reduction of *p*-chloronitrobenzene on illuminated nano-titanium dioxide particles

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Abstract

The photocatalytic reduction of *p*-chloronitrobenzene in titanium dioxide slurries in the absence of oxygen and in the presence of the sacrificial electron donors under UV light irradiation was investigated in the present study. TiO_2 used were A101, P25, and R201. The sacrificial electron donors consisted of isopropanol, methanol, ethanol, formic acid, etc. The results of photocatalytic reduction reaction were monitored with HPLC method by identifying reduction products. The effects of reduction time, properties and loading of TiO_2, concentration of substrate, types and ratio of photogenerated hole scavenger on reductive rate and yield of *p*-chloroaniline were evaluated. *p*-Chloroaniline yield could reach high up to 99.20% in 12 h for P25 used, while for A101 it was 68.22% and for R201 only 15.06%. In general, P25 was the best one of all the catalysts used. The mixture of *i*-propanol and formic acid (v:v = 90:10) was selected as reductive medium because of less by-product and higher *p*-chloroaniline yield.

Keywords: Photocatalytic reduction; Chloronitrobenzene; Titanium dioxide; Ultraviolet light; Irradiation; Chloroaniline; *i*-Propanol

1. Introduction

When a semiconductor such as TiO_2 absorbs photons with wavelength less than 387 nm, and is promoted to an excited state, an electron is transferred from the valence band (VB) of the semiconductor to the conduction band (CB), where it can function as a reducing agent, and leaves an electronic vacancy behind [1]. Nowadays, researches focused on photocatalytic reduction have been more and more popular, with reduction of metal ions mainly involved, such as photocatalytic reduction of toxic heavy metal ions (Cr^{6+}, Hg^{2+}, Pb^{2+}, Se^{6+}) [2,3]; photocatalytic deposition and recovery of precious metal (Ag, Au) [4]; deposition of metal particles on supporter for activating catalysts (Pt, Pd) [5], and so on. There are only a few reports on the reduction of organic compounds. Satisfactory yields can be obtained when the method of photocatalytic reduction with TiO_2 as a catalyst applied to a series of aromatic nitrocompounds [1,6,7]. When an alcohol is used as a sacrificial electron donor, it is suggested that the photogenerated hole in the VB of an excited semiconductor can cause oxidation of an alcohol to a corresponding carbonyl compound, hydrogen, and a proton as illustrated in Fig. 1. Besides the electron generated, the hydrogen produced during the above-mentioned process can also cause the reduction of nitro compounds. Usually, the nitro compound is completely reduced to its amino derivative in the absence of oxygen [6]. Photoinduced reduction of nitro compounds using semiconductor particles as catalysts is now an emerging and promising technology in view of pursuing environmentally 'benign' or 'green' synthesis, since it uses solar-driven photocatalysts whose chemistry is initiated by the absorption of low energy photons, and occurs at atmospheric pressure and room temperature. In

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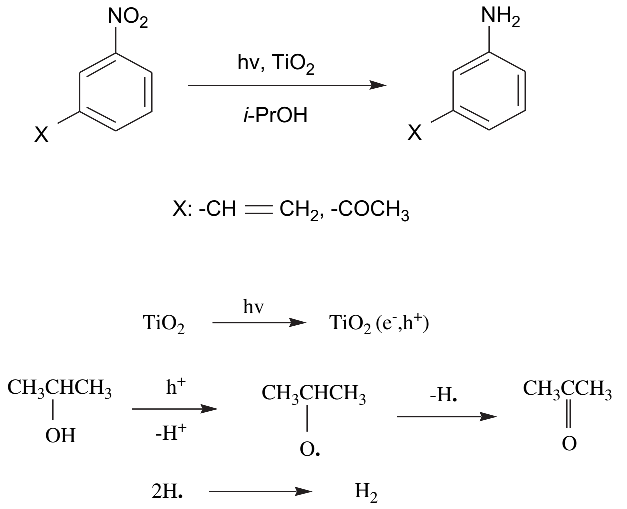

Fig. 1. A mechanism of photocatalytic reduction of organic nitro compounds in the presence of an alcohol [6].

addition, the procedure is much simpler than some other literature procedures for the preparation of some amino compounds from their nitro compounds. Of all the semiconductors, titanium dioxide has been widely used for its high stability, non-toxicity, and its ability to be reused after the recycle from the reaction medium.

p-Chloroaniline (PCA) is a main raw material and intermediate for the synthesis of rubber, dyes, medicines, pesticides and photographic materials. With the science and technology development, more and more extensive attentions have been paid on the applications of PCA in chemical engineering, pharmaceuticals and printing industries. PCA is mainly prepared by the reduction of *p*-chloronitrobenzene (PCNB). The reductive methods include: (1) reduction by using iron–ammonium chloride [8]; (2) reduction with sulfides [9,10]; (3) electrochemistry reduction [11]; (4) reduction under carbon monoxide [12]; (5) catalytic hydrogenation [13,14]; (6) reduction by activated metals [15,16]; (7) reduction by borohydrides [17–19]; (8) reduction by sodium hydrogen selenide [20]; (9) solvent-free reduction of PCNB with hydrazine under microwave irradiation [21]. But the method of photocatalytic reduction of PCNB has not been investigated. Here, we report the photocatalytic reduction of PCNB to PCA using TiO_2 as a catalyst, and the main factors influencing the yield of PCA are involved. We have found that PCNB could be reduced to PCA in higher yield in the presence of nanometer TiO_2 under UV light irradiation.

2. Experimentals

2.1. Materials

A101 (commercial titanium dioxide product, anatase 99.1%, $\bar{d} = 215$ nm), R201 (commercial titanium dioxide product, rutile 95.3%, $\bar{d} = 167$ nm), were obtained from Zhonghe Huayuan Taibai (China, ZHTC); P25 (commercial titanium dioxide, anatase ca. 86.2%, rutile ca. 13.8%, $\bar{d} = 50$ nm) was provided by Degussa Co. as a gift; PCNB, formic acid (HCOOH), methanol (MeOH) were obtained from Beijing Jinlong Chemical Reagent Co.; isopropanol (*i*-PrOH), ethanol (EtOH) were obtained from Tianjin No.2 reagent factory. All reagents were used without further purification. A101 was mainly used in most of the experiments in this study in order to evaluate the photoreductive ability of nano-titanium dioxide made in China. Additionally, comparisons were made about the photocatalytic capacity of A101, R201 and P25.

2.2. Reduction procedure

In a 120 mL Pyrex glass jacketed reactor (Fig. 2) equipped with a magnetic stir bar, 10 mL HCOOH, 90 mL *i*-PrOH, 0.63 g PCNB, 0.64 g A101 TiO_2 particles were mixed and suspended. The reactor was then sealed with a rubber septum. The suspension was stirred and purged with nitrogen for 1.5 h, then it was irradiated under a high-pressure mercury lamp (100 W). The temperature in the reactor was kept 25 ± 2° C by the circulating water. At given irradiation time intervals, liquid samples were taken from the suspension and treated with centrifugal separation, then filtered with 0.2 μm membrane filter to remove TiO_2 particles. The resulting filtrate was injected into high performance liquid chromatograph (HPLC) for product identification and yield calculation.

2.3. Analytical method

PCA and PCNB were identified by HPLC and confirmed by comparing the retention time with authentic

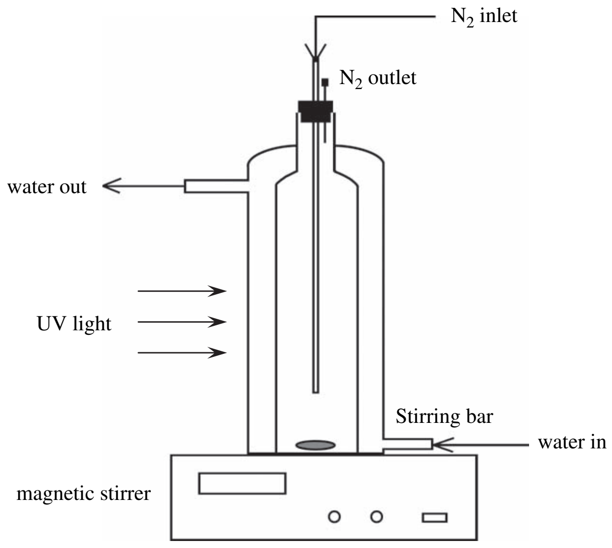

Fig. 2. The reactor for photocatalytic reduction.

samples. External standard method was used for quantitative analysis. Instrument: Agilent 1100 series (HPLC, U.S.A); separation column: Zorbax Eclipse XDB-C8, 4.6 × 150 mm, 5-micron; mobile phase: 70% MeOH and 30% water (v:v); flow rate: 1.0 mL/min; sample volume injected: 10 μL; detection wavelength: 260 nm.

3. Results and discussion

3.1. Solvent effect

The photocatalytic reduction of organic electron acceptors can be carried out in the presence of a large excess of a sacrificial electron donor. The function of the sacrificial electron donor is to scavenge valence band holes, thereby decreasing the recombination degree of photogenerated electron and hole, and freeing more reductive equivalents [1]. A lot of solvents, such as EtOH [6], MeOH, *i*-PrOH [1], HCOOH [3], have been reported as useful sacrificial electron donor in improving reduction efficiency. Ferry and Glaze [1] investigated the mechanism of photocatalytic reduction of some nitroaromatic compounds at the surface of TiO_2 slurries (P25) in the presence of the sacrificial electron donor MeOH or *i*-PrOH, and revealed that secondary radicals generated from alcohol oxidation play no role in the observed reduction kinetics. Furthermore, photocatalysts surface should be responsible for the photocatalytic reduction.

For the reduction of PCNB in the present study, various solvents were chosen to vary the reduction yield. It was shown that solvent played a quite remarkable role in the conversion of PCNB and the yield of PCA. The by-products, of which the structures were not identified, consisted of several single compounds. For the purpose of evaluation of by-products production and the convenience of study, we calculated the values recognized as relative values of by-products for further comparisons by dividing the total area of all the peaks in a chromatograph by the total peak area of all by-products. Table 1 presents the effect of different solvents on the reduction of PCNB. As for runs 1–4, pH was not detected, which was assumed to be around 7. In run 1, MeOH was selected as the solvent. The PCNB conversion was 32.06%, while the PCA yield was low to about 6% and by-products high to 29.49%. In runs 2 and 3, mixture of EtOH and water was chosen. The PCA yield was higher than that in run 1; the PCNB conversion and PCA yield decreased with the increase amount of water. In run 4, we gained higher yield and lower by-product than those in former runs by using *i*-PrOH as the solvent. So the study was furthered on more reductive results using *i*-PrOH.

It is usually thought that pH has an effect on the result of photocatalytic reactions. Compared to Cl^- and SO_4^{2-} that often lower the rate of the reaction, ClO_4^- always shows less influence [22]. So $HClO_4$ was chosen to adjust the pH of *i*-PrOH system to 4 (run 5). Compared with the results in run 4, PCNB conversion and by-product increased significantly for run 5, while PCA yield decreased. This result showed that pH plays a negative role in PCA production. In run 6, oxalic acid (also a sacrificial electron donor often used [23]) was added to *i*-PrOH system, which made pH lower to 4. However, PCNB conversion and PCA yield were not improved. In run 8 the solvent was totally consisted of HCOOH, but PCNB conversion and PCA yield were very low. When the mixture of formic acid and *i*-PrOH was used as solvent in run 7, PCNB conversion and PCA yield were significantly improved to 80.08% and 68.22%. Though HCOOH addition also lowered the pH to 4, maybe its function to scavenge valence band holes is much more effective. Thus, *i*-PrOH with small amount of HCOOH is the best solvent because of less by-product and higher PCA yield. It made us choose the

Table 1
The effect of solvents on photocatalytic reduction[a]

Run	Solvent	Amount (mL)	pH[b]	Time (h)	Conversion[c] (%)	Yield[d] (%)	By-product[e] (%)
1	MeOH	100	/	12	32.06	6.29	29.46
				16.7	65.87	6.41	49.32
2	EtOH:H_2O	30:70	/	8	30.12	11.50	14.76
3	EtOH:H_2O	95:5	/	12	47.02	17.99	35.34
4	*i*-PrOH	100	/	7	20.26	16.70	11.82
				12	29.32	20.62	14.94
5	*i*-PrOH	100	4($HClO_4$)	12	41.9	17.08	35.76
6	*i*-PrOH	100	4($(HOOC)_2$)	12	35.79	15.10	14.70
7	*i*-PrOH:HCOOH	90:10	4	12	80.08	68.22	10.83
8	HCOOH	100	4	12	20.42	18.51	16.34

[a] The initial concentration of PCNB was 6.3 g/L (except run 2, 12.6 g/L). Photocatalyst was A101 for all the runs.

[b] The pH of runs 6, 7 and 8 were initial values after adding acid as electron donor, not adjusted purposely. The pH of run 5 was adjusted by adding $HClO_4$ to make comparison with that of run 4 on the effect of pH.

[c] The conversion of PCNB.

[d] The yield of PCA.

[e] The values were obtained by dividing the total area of all the peaks in a chromatograph by the peak area of all the by-products.

mixture of *i*-PrOH with HCOOH (v:v = 90:10) as the solvent in the following reactions.

3.2. The photocatalysis of TiO_2 for PCNB

Several control experiments were done to evaluate the photocatalytic function of TiO_2. Table 2 describes that experiments without light or TiO_2 gave negligible amount of PCA product, and the one under UV irradiation without TiO_2 can only offer the PCA yield of 29.50% (irradiation time 12 h). Compared with the yield of the experiment under the condition of light on and TiO_2, we can conclude that TiO_2 as a photocatalyst plays an effective role in the process of reduction. Higher yields of PCA with irradiation (no TiO_2) were obtained than that without irradiation (in the absence of TiO_2). Maybe it is due to the photochemical characteristic of HCOOH. We have no sufficient explanation for it.

3.3. Effect of TiO_2 concentration

The effect of TiO_2 concentration on the reduction of PCNB is drawn in Fig. 3. With increasing concentration of TiO_2, the reduction process was accelerated (the higher yield of PCA under the same time of irradiation reached). At low TiO_2 concentrations (<2 g/L), the reduction rate increases sharply with the TiO_2 concentration increase; when the TiO_2 concentrations are higher than 2 g/L, the increase of reduction rate become smooth and approached a limiting value. It can be concluded that TiO_2 concentration has powerful effect on reduction rate at low concentrations. When more TiO_2 particles are contained in the suspensions, they will adsorb more protons to accelerate the reduction process. But if the TiO_2 particles are much more than needed, the extra TiO_2 suspended in the mixture will prevent the transmission of light and enhance the reflection of light, which makes the particles far from the light source not to be efficiently excited, thus the effect of the TiO_2 concentration become negligible. This result is consistent with the consequences of many previous documents [24].

3.4. Effect of the initial concentrations of PCNB

The effect of the initial PCNB concentrations on the yield of PCA is shown in Fig. 4. With increasing concentrations of PCNB, the PCA yield becomes lower under the same time of irradiation. This may be attributed to the increasing amount of adsorbed PCNB (not measured in the experiment) involved in the reduction that has produced absolute increasing amount of PCA. While the TiO_2 concentration and the light intensity remain the same, the protons adsorbed by TiO_2 are constant. As a result, the increasing amount of PCA is limited compared to the initial PCNB concentration, which lowered the total yield. It means that the photocatalytic reduction of PCNB is not a simple first-order reaction as with other semiconductor photo-assisted degradation, following the typical Langmuir–Hinshelwood model (related to adsorption and reaction).

Table 2
The comparison of reaction results in the presence (absence) of TiO_2 (A101)

Condition	TiO_2 (g/L)	Time (h)	Yield of PCA (%)
Light off	/	6.5	0.37 (N_2 purged)
		11.2	0.29 (N_2 purged)
Light on	/	9	19.46
		12	29.50
Light on	6.4	12	68.22

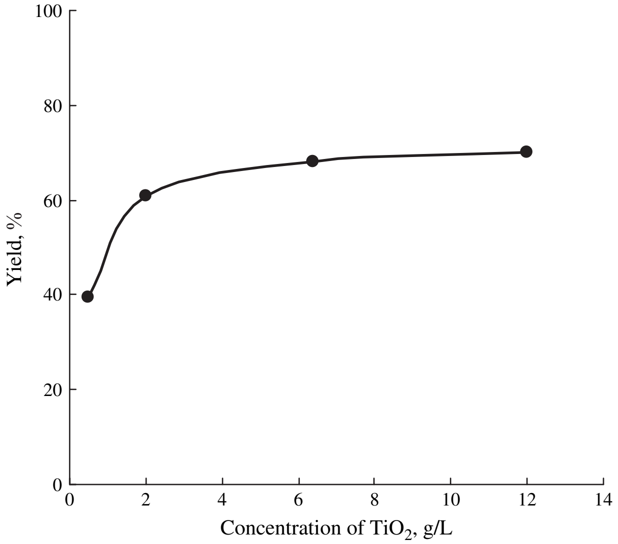

Fig. 3. The yield of PCA as a function of TiO_2 concentration. $[PCNB]_0$ = 6.3 g/L; *i*-PrOH:HCOOH = 90:10 (v:v); Time = 12 h.

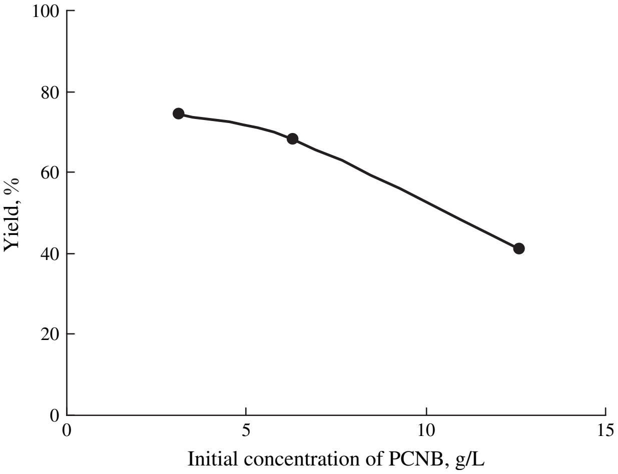

Fig. 4. The yield of PCA as a function of the PCNB concentration. $[TiO_2]$ = 6.4 g/L; *i*-PrOH:HCOOH = 90:10 (v:v); Time = 12 h; Catalyst = A101.

3.5. Time course of the photocatalytic reduction

Fig. 5 shows that the yield of PCA increases nearly proportionally to the irradiation time within 12 h. The dark reaction is nearly negligible during the time interval (1.5 h). The yield reached 68.22% finally and peak area percentage of by-product in a chromatograph is less than 10%, which demonstrates that PCA is the principal product of the photocatalytic reaction. It is also predicted that the yield of PCA will continue to rise if the irradiation time is prolonged.

3.6. Effect of HCOOH concentrations

The dependence of the PCNB reduction upon the HCOOH concentration is illustrated in Fig. 6. Adsorption of some species that can trap electrons or holes plays an important role in heterogeneous photocatalysis. At high HCOOH concentration (or complete replacement of *i*-PrOH by HCOOH) the PCA yield was unsatisfactorily low (about 20%). The formate adsorption had reached saturation on the surface of TiO_2 in these cases, but PCNB adsorption was too less (both adsorptions were not determined). On lowering the HCOOH concentration the PCA yield reached a maximum of 68.22% at the percentage of HCOOH 10%. At even lower HCOOH concentrations (<10%), the yield of PCA increased sharply with the increase in HCOOH concentration. The expression may be the same as the mechanism of photocatalytic reduction of inorganic NO_3^- [25], Se^{4+}, Se^{6+} [3] and nitroaromatic compounds [26] using HCOOH. Reducing radicals $^{\bullet}COO^-$ and $R-{}^{\bullet}CH-OH$ are formed when HCOOH and alcohol are oxidized by hydroxyl radicals or the photogenerated holes, and the former has the stronger reductive ability [3]. Increasing amount of formate, which is an effective photogenerated hole scavenger, will accelerate considerably the reaction rate of photocatalytic reduction when it is effectively adsorbed on the surface of TiO_2 powder. But if the concentrations of formate are much higher than that needed, it will compete adsorption on the surface of TiO_2 with PCNB and make the latter unable to accept electrons from the conduction band directly. Subsequently, the process of PCNB adsorption will dominate the reduction step. Therefore, an optimum HCOOH concentration occurs for the photocatalytic reduction of PCNB. It is very similar with the photocatalytic reduction of Se^{6+} in the presence of HCOOH [3b].

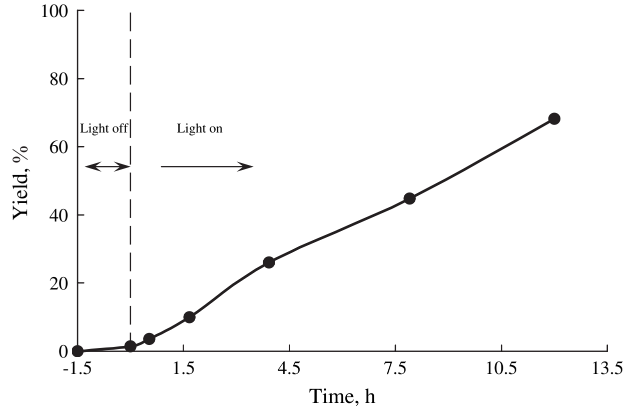

Fig. 5. Time course of the photocatalytic reduction. $[TiO_2] = 6.4$ g/L (A101); *i*-PrOH:HCOOH = 90:10 (v:v); $[PCNB]_0 = 6.3$ g/L.

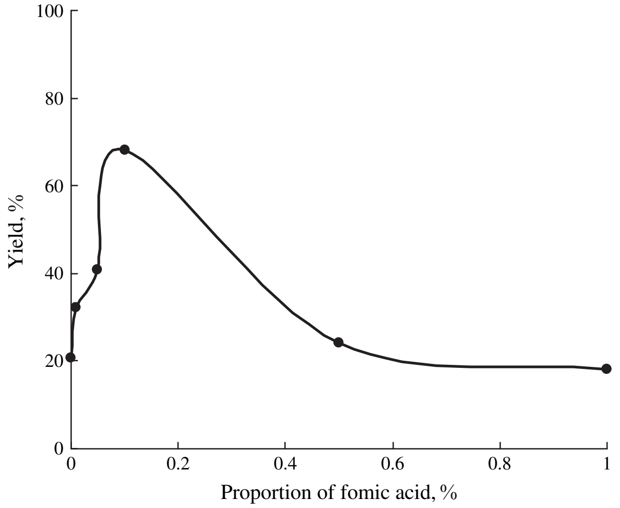

Fig. 6. The yield of PCA as a function of the formic acid concentration. $[TiO_2] = 6.4$ g/L (A101); total volume of mixed solvent = 100 mL; $[PCNB]_0 = 6.3$ g/L; Time = 12 h.

3.7. Effect of different TiO_2 catalysts

Table 3 describes the effect of three different catalysts on the yield of PCA. P25 was the best one of the three. Compared with A101, P25 has smaller particle size and larger specific surface area, which may lead to much higher reductive capacity and better selectivity. By using it the highest yield, least amount of by-product, highest rate can all be obtained. R201 (rutile) has the worst photochemical activity.

Table 3
Differences of photocatalysis on TiO_2 kinds

Run	TiO_2	Manufacturer	Anatase (%)	Rutile (%)	$\bar{d}$ (nm)	Time (h)	Yield (%)
1	A101	ZHTC	99.1	0.9	215	12	68.22
2	R201	ZHTC	4.7	95.3	167	12	15.06
3	P25	Degussa	86.2	13.8	50	3.78	98.00
						12	99.20

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