

## Novel Redox Photocatalyst Pt–TiO<sub>2</sub> for the Synthesis of 2-Methylquinolines from Nitroarenes

Kaliyamoorthy Selvam and Meenakshisundaram Swaminathan\*

Department of Chemistry, Annamalai University, Annamalainagar 608 002, India

Received March 25, 2011; E-mail: chemres50@gmail.com

An eco-friendly and efficient procedure for synthesis of 2-methylquinoline derivatives from nitroarenes has been developed by a simple one-pot reaction on the surface of platinum-loaded TiO<sub>2</sub> with neat ethanol under UV irradiation without any harsh reagent according to green chemistry. TiO<sub>2</sub> catalysts with various amounts of Pt loadings were prepared by photodeposition using chloroplatinic acid solution and characterized by XRD, BET, AFM, HR-TEM, XPS, and DRS. XRD patterns showed that the crystal structure of Pt–TiO<sub>2</sub> still remained as anatase phase. The UV–vis spectra indicated that Pt promoted the absorption of visible light. The XPS measurements reveal that platinum particles are present mainly in metallic form. AFM and HR-TEM analysis revealed the presence of nonspherical shaped platinum nanoparticles of the diameter 3–12 nm. Pt–TiO<sub>2</sub> on irradiation induces a combined redox reaction with nitroarene and alcohol and this is followed by condensation–cyclization of aniline and oxidation products to give 2-methylquinolines.

In the last few years heterogeneous photocatalysis applied to synthetic chemistry has become an exciting and rapidly growing area of research. For a multistep synthesis, illuminated semiconductors offer unique features. Many studies have reported photocatalytic organic reactions using mild experimental conditions.<sup>1–3</sup> To date they are mostly in the categories of oxidation and oxidative cleavage, reduction, geometric and valence isomerization, substitution, condensation, and polymerization.<sup>3</sup> A major drawback in TiO<sub>2</sub> photocatalyzed reaction is the recombination of photogenerated electron–hole pair. This energy wasting step can be inhibited by incorporating noble metals as electron acceptor on TiO<sub>2</sub>. The deposition of noble metals, such as Pt, Pd, Ru, and Au onto the surface of TiO<sub>2</sub> can increase the efficiency of photocatalytic reactions (degradation as well as production of hydrogen gas).<sup>4–6</sup>

In previous studies, it has been reported that platinum is one of the most active metals for photocatalytic enhancement and it can produce the highest Schottky barrier among the metals that facilitate electron capture.<sup>7</sup> Photogenerated electrons migrate to the metal, where they become trapped and the electron–hole pair recombination is suppressed. The discovery of the photo-Kolbe reaction by Kraeutler and Bard using Pt/TiO<sub>2</sub> as a photocatalyst for the conversion of acetic acid to methane and CO<sub>2</sub> has attracted much attention.<sup>8</sup> However in spite of several semiconductor mediated reactions, examples of combined redox reactions are rather limited in the literature.<sup>9–12</sup> The fact that some chemical reactions occur only in photocatalytic systems is more significant for this application.

Quinoline and its derivatives have been the subject of much research due to their importance in various applications and their widespread biochemical significance. A large variety of quinoline derivatives have been used as antimalarial, anti-inflammatory, antiasthmatic, antibacterial, antihypertensive, and tyrosine kinase PDGF-RTK inhibiting agents.<sup>13–15</sup> Many synthetic methods such as Skraup, Doebner–von Miller, Friedländer, and

Combes reactions have been developed for the preparation of quinolines.<sup>16–19</sup> However these methods are not fully satisfactory with regard to operational simplicity, cost of the reagent, and isolated yield. Thus, the drive continues to find a better and improved methodology.

Faraway from thermal synthetic routes to quinolines, very few studies on photocatalytic cyclization of nitrobenzene and its derivatives have been carried out to yield corresponding substituted quinolines and tetrahydroquinolines. A number of photocatalysts such as TiO<sub>2</sub>, TiO<sub>2</sub> with a cocatalyst (*p*-toluenesulfonic acid) and others have been used.<sup>20–22</sup> Recently, we have reported the use of Au–TiO<sub>2</sub> for the photocatalytic conversion of anilines and its derivatives into corresponding 2-methylquinolines under UV light.<sup>23</sup> But the method of photocatalytic conversion of nitroaromatics to 2-methylquinolines with Pt–TiO<sub>2</sub> has not been investigated. We wish to report herein our results on a combined redox methodology that leads to a facile and selective synthesis of 2-methylquinolines from nitroarene and ethanol under mild reaction conditions using Pt–TiO<sub>2</sub>. The reported procedure for synthesis of 2-methylquinolines is much simpler and more efficient.

### Experimental

**Materials and Methods.** All chemicals were of the highest purity available and were used as received without further purification. Dihydrogen(hexachloroplatinate) dihydrate (H<sub>2</sub>[PtCl<sub>6</sub>]·2H<sub>2</sub>O) (Aldrich) was used as Pt source. Nano TiO<sub>2</sub> was prepared by the hydrolysis of titanium tetraisopropoxide (Himedia 98.0%), in isopropyl alcohol solution (1.6 M) by the addition of distilled water (isopropyl alcohol–water 1:1). The resulting colloidal suspension was stirred for 4 h. The gel obtained was filtered, washed and dried in an air oven at 100 °C for 12 h. The sample was calcinated at 400 °C in a muffle furnace for 12 h. The metal-loaded TiO<sub>2</sub> catalyst was prepared by photoreduction of metal ions on TiO<sub>2</sub> as per the procedure

reported in our previous paper.<sup>24</sup> Pt(*x*)-TiO<sub>2</sub> samples, containing different platinum loadings [*x* (wt %) = Pt/(TiO<sub>2</sub> + Pt)100; *x* = 0.5, 1.0, 1.5, and 2.0%] were prepared.

**Apparatus.** X-ray diffraction (XRD) patterns of TiO<sub>2</sub> and Pt-TiO<sub>2</sub> powder samples were obtained using a Model D/Max 2550V with Cu anticathode radiation. The diffractograms were recorded in 2θ range between 10 and 80° in steps of 0.02° with count time of 20 s at each point. The crystalline phase can be determined from integration intensities of anatase (101), rutile (110), and brookite (120) peaks and the average crystallite sizes were determined according to the Debye-Scherrer equation using the full width half maximum data of each phase.

$$D = K\lambda/\beta \cos \theta \quad (1)$$

Where *D* is the crystal size of the catalyst, *λ* is the X-ray wavelength (0.154 nm), *β* is the full width half maximum (FWHM) of the catalyst, *K* = 0.89, and *θ* is the diffraction angle.

The phase formation, particle size, surface morphology, and crystallinity of pure and loaded catalysts were examined using transmission electron microscopy (TEM) (Model JEOL TEM-3010) operated at 300 keV. The samples for TEM analysis were prepared by dispersion of the catalysts in ethanol under sonication and deposition on a copper grid. High-resolution TEM (HR-TEM) measurements were carried out using a JEOL-JEM-2010 UHR instrument operated at an acceleration voltage of 200 kV with a lattice image resolution of 0.14 nm. X-ray photoelectron spectra (XPS) of the catalysts were recorded with an ESCA-3 Mark II spectrometer (VG Scientific Ltd., England) using Al Kα (1486.6 eV) radiation as the source. The spectra were referenced to the binding energy of C(1s) (285 eV).

The DRS of all the catalysts were recorded on a Shimadzu UV 2450 model UV-visible spectrophotometer in the range of 800–190 nm equipped with an integrating sphere and using powdered BaSO<sub>4</sub> as a reference. Reflectance spectra were converted to the absorbance spectra using the Kubelka-Munk equation

$$F(R_{\infty}(\lambda)) = \frac{(1 - R_{\infty})^2}{2R_{\infty}} \quad (2)$$

The specific surface areas of the catalysts were determined using a Micromeritics ASAP 2020 sorption analyzer. The samples were degassed at 423 K for 12 h and analysis was performed at 77 K with N<sub>2</sub> gas as the adsorbate. The Brunauer-Emmett-Teller (BET) multipoint method least-squares fit provided the specific surface area.

To study the morphology of catalyst, an atomic force microscope (AFM) JSPM-5200TM, JEOL model was used. This AFM uses a silicon tip with a radius of 20 nm and a low-resonance frequency cantilever that has a manufacturer's spring constant of 35–65 N m<sup>-1</sup>. Scans of 1.8 × 1.8 μm were obtained for each sample. The images were recorded in the noncontact mode. All recordings were made in air under ambient conditions to produce 2D and 3D images.

**Photocatalytic Synthesis of 2-Methylquinolines.** In a typical experimental run, 50 mg 1.5%Pt-TiO<sub>2</sub> was suspended in 25 mL of an absolute ethanolic solution containing 25 mM of the nitrobenzene and irradiated by a 365 nm medium-pressure mercury lamp (Sankyo Denki, Japan; intensity *I* = 1.381 ×

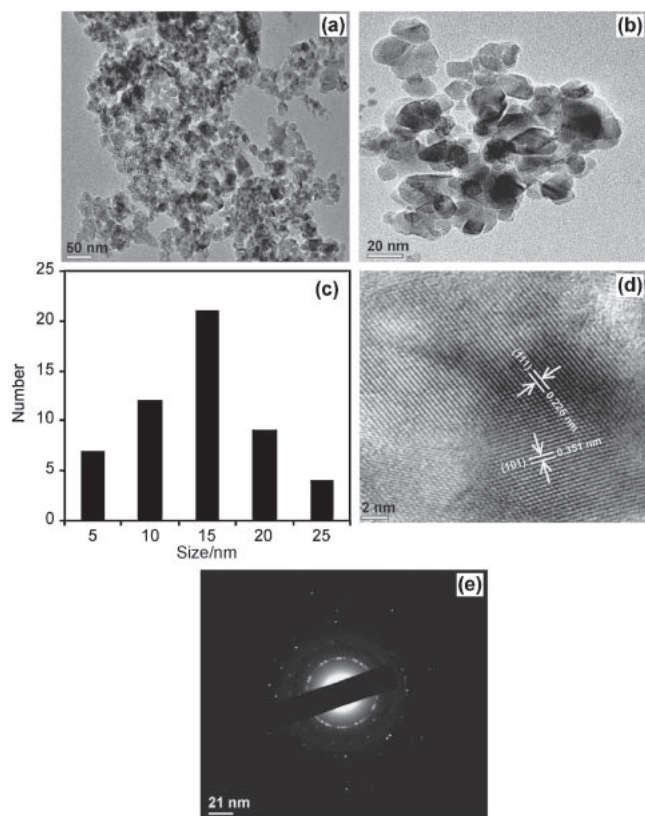
10<sup>-6</sup> einstein L<sup>-1</sup> s<sup>-1</sup>) after purging with N<sub>2</sub> for 30 min. N<sub>2</sub> bubbling (flow rate = 6.1 mL s<sup>-1</sup>) and magnetic stirring of the suspension were continued throughout the reaction while the temperature was maintained at 30 ± 1 °C. Progress of the reaction was monitored by TLC. Product analysis was performed by GC analysis, Perkin-Elmer GC-9000 with a capillary column of DB-5 and flame ionization detector was used. GC/MS analysis was carried out using a Varian 2000 Thermo with the following features: capillary column VF5MS (5% phenyl-95% methylpolysiloxane), 30 m length, 0.25 mm internal diameter, 0.25 μm film thickness, temperature of column range from 50 to 280 °C (10 °C min<sup>-1</sup>), and injector temperature 250 °C, attached to mass spectrometer model SSQ 7000. The isolation was performed by column chromatography on a silica gel column by eluting with a cosolvent of hexane and ethyl acetate (volume ratio: 8:2).

## Results and Discussion

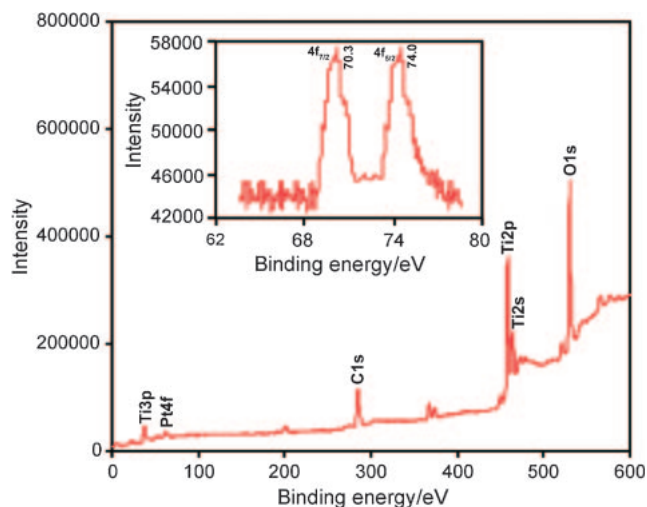
**Catalyst Characterization.** Pt-loaded TiO<sub>2</sub> (1.5 wt % Pt) catalyst was characterized by X-ray diffraction (XRD), BET surface area, atomic force microscopy (AFM), transmission electron microscopy (TEM), and diffuse reflectance spectroscopy (DRS). The XRD pattern of prepared TiO<sub>2</sub> is identical with the standard pattern of anatase (JCPDS 01-078-2486 C), and rutile lines (01-089-0553 C) are absent. The peaks at 25.43, 37.92, 48.03, 53.97, 55.05, 62.70, 68.80, 70.39, and 75.05° are the diffractions of the (101), (004), (200), (105), (211), (204), (116), (200), and (215) crystal planes of anatase TiO<sub>2</sub>, respectively (Figure S1). These results confirm that photo-deposition of the platinum does not modify the basic crystal structure of the TiO<sub>2</sub> used (tetragonal, *a* = 0.37845 nm, *c* = 0.95143 nm, body centered). The diffraction patterns of the Pt-TiO<sub>2</sub> samples do not show XRD peaks of metallic platinum at 39.76, (111); 67.71°, (220); etc. This may be because of either homogeneous dispersion of discrete platinum deposits in the nanoscale on the surface of the TiO<sub>2</sub> or because of very low platinum content.

In Figure S2 an AFM 3D image of a dense Pt-loaded TiO<sub>2</sub> nanoparticle is shown. Pt-TiO<sub>2</sub> particles are well dispersed without any trace of coalescence. Consequently we can be assured that Pt particles in TiO<sub>2</sub> layer are either overcoated or sandwiched.

TEM images at two different regions permit easy differentiation of Pt loading in TiO<sub>2</sub> crystallites (Figures 1a and 1b). Pt nanocrystals are seen on the surface of the TiO<sub>2</sub> particle as dark dots. The particle size of Pt-TiO<sub>2</sub> nanoparticles has been analyzed in HR-TEM and shown in Figure 1c. It can be seen that the size of Pt-TiO<sub>2</sub> particles are in the range from 5 to 25 nm with an average particle size of 14.8 nm. Pt metal particles are randomly dispersed on the TiO<sub>2</sub> surface. Further observations from high-resolution TEM micrograph show that the Pt particles diameters are in the range of 3–12 nm and randomly located on the crystal surface. Figures 1d and 1e show the lattice fringes of Pt and TiO<sub>2</sub> and SAED pattern of Pt-TiO<sub>2</sub>. The distance between the fringes is measured with analysis software included in the instrument. The statistical *d*-value is 0.225 nm for the Pt particles and 0.351 nm for the TiO<sub>2</sub> crystals, indicating that the observed fringes are for the Pt(111) plane and TiO<sub>2</sub>(101) anatase facets, respectively.



**Figure 1.** HR-TEM analysis: (a and b) images of Pt-TiO<sub>2</sub>, (c) particle size distribution of Pt-TiO<sub>2</sub>, (d) lattice fringes of Pt-TiO<sub>2</sub>, and (e) SAED pattern of Pt-TiO<sub>2</sub>.



**Figure 2.** X-ray photoelectron spectra of Pt-TiO<sub>2</sub>.

The electronic state of Pt in the catalysts was analyzed by XPS. The XPS survey spectrum (Figure 2) of the Pt-TiO<sub>2</sub> indicates the peaks of elements Ti, O, C, and Pt (trace). The carbon peak is attributed to the residual carbon from the sample and adventitious hydrocarbon from the XPS instrument itself. The Ti2p peak at 461 eV, O1s peak at 534 eV, and Pt4f peak at 70.3 eV reveal the presence of Ti, O, and Pt elements in Pt-TiO<sub>2</sub>. A high-resolution XPS spectrum (inset Figure 2) from 62 to 80 eV confirms the existence of Pt. Figure 2 shows the

binding energies of Pt4f<sub>7/2</sub> (70.3 eV) and Pt4f<sub>5/2</sub> (74.0 eV) and the splitting of the 4f doublet (3.7 eV). These binding energies indicate that platinum is present in metallic state.

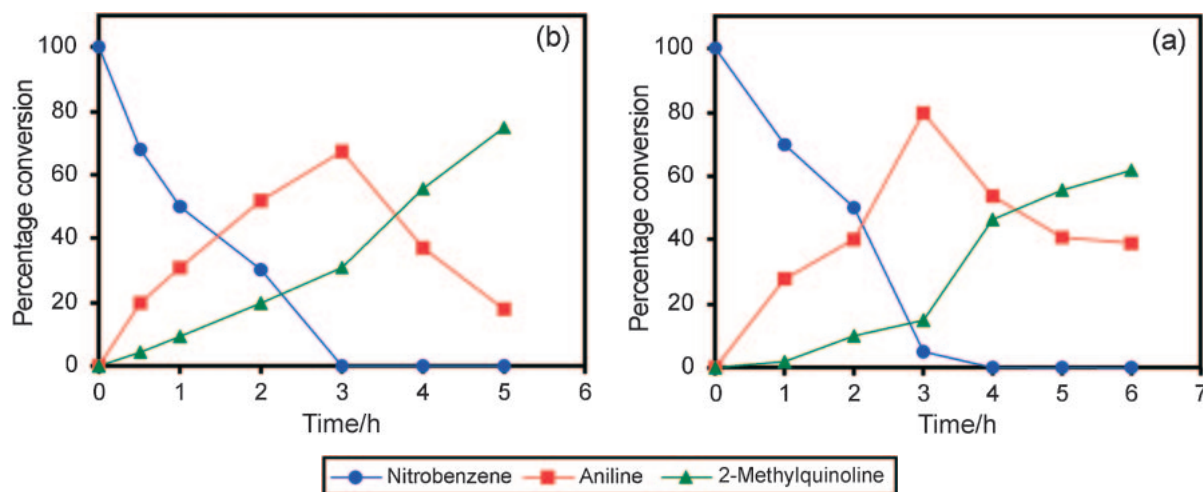
N<sub>2</sub> adsorption and desorption studies show the isotherms as type II (Figure S3). This type of isotherm is indicative of nonporous materials. Surface area measurements, made by the BET method, provide the specific surface areas of Pt-TiO<sub>2</sub> and prepared TiO<sub>2</sub> as 64 and 74 m<sup>2</sup> g<sup>-1</sup>, respectively. The specific pore volume of Pt-TiO<sub>2</sub> sample (0.995: 0.243 cm<sup>3</sup> g<sup>-1</sup>) shows that the Pt-TiO<sub>2</sub> is nonporous.

The diffuse reflectance spectrum of 1.5% Pt-doped shows an increased absorption in the visible region (Figure S4). The reflectance data reported as  $F(R)$  values have been obtained by application of the Kubelka-Munk algorithm. The band gap of the doped oxide has been deduced from the Tauc plot of  $[F(R)h\nu]^{1/2}$  versus photon energy (Figure S5) as 3.02 eV.

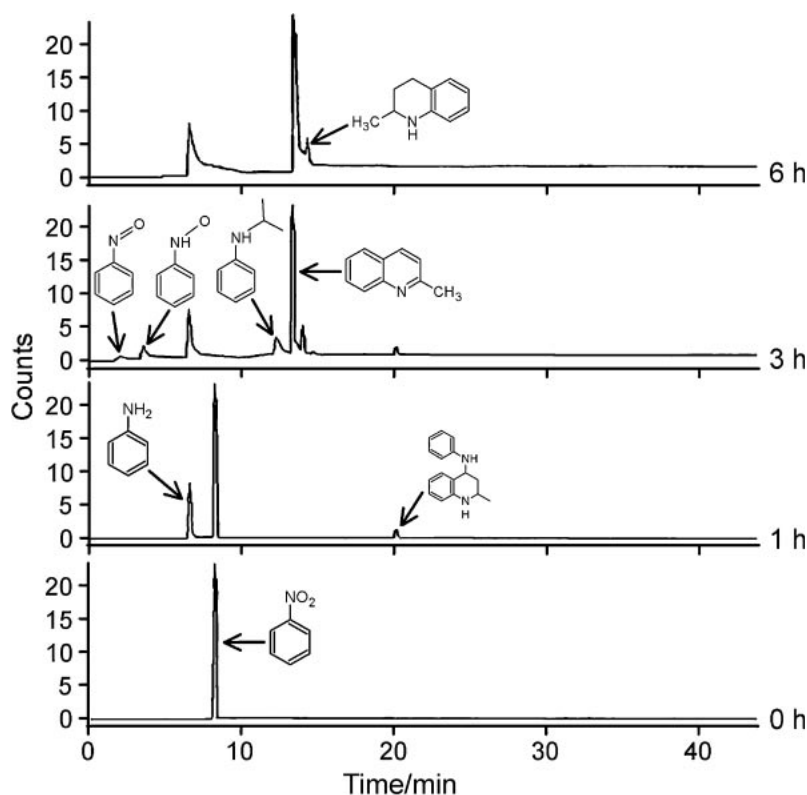
**Photocatalytic Synthesis of 2-Methylquinoline from Nitrobenzene.** Initial experiments were carried out with ethanolic solutions of nitrobenzene containing TiO<sub>2</sub> nanoparticles under different conditions. Irradiation of nitrobenzene and TiO<sub>2</sub> in ethanol with 365 nm UV light produced cyclized product of 2-methylquinoline. Neither the irradiation of ethanolic solution of nitrobenzene alone nor the solution of nitrobenzene and the catalyst without light gave any product. This indicates that both light and TiO<sub>2</sub> are essential for the formation of 2-methylquinoline. The catalytic activity of Pt-TiO<sub>2</sub> for the synthesis of 2-methylquinoline **2** was investigated for the reaction of nitrobenzene **1** with ethanol. The changes in the concentrations of **1** and the product, 2-methylquinoline **2** during the photocatalytic reaction were determined at different times. With pure TiO<sub>2</sub> (Figure 3a), 6 h photoirradiation was required to achieve >99% consumption of **1**, affording **2** in only ca. 60% yield. The yield was determined by comparison with the retention times of authentic samples and by coinjection with the authentic compounds. The main product identified was 2-methylquinoline. In contrast, Pt-TiO<sub>2</sub> promoted the rapid and selective production of **2** by achieving 99% consumption of **1** with only 5 h irradiation to afford **2** in 70% yield (Figure 3b). This indicates that Pt-TiO<sub>2</sub> promotes rapid and selective 2-methylquinoline production.

The higher efficiency and selectivity of Pt-TiO<sub>2</sub> was also shown by the formation of products from 3-methylnitrobenzene, 4-methylnitrobenzene, and 4-methoxynitrobenzene. Pt-TiO<sub>2</sub> produced 74, 76, and 68% of substituted 2-methylquinolines but bare TiO<sub>2</sub> gave only 68, 47, and 41.0% from 3-methylnitrobenzene, 4-methylnitrobenzene, and 4-methoxynitrobenzene respectively (data not shown). This indicates that Pt-TiO<sub>2</sub> promotes rapid and selective production of substituted 2-methylquinolines.

The higher conversion of nitrobenzene with Pt-TiO<sub>2</sub> is due to the trapping of electrons by Pt on the excited TiO<sub>2</sub>. The electrons excited from the valence band of TiO<sub>2</sub> to the conduction band are efficiently transferred to Pt (charge separation effect) and accumulated therein (electron pool effect). The oxidant (alcohol) and the reductant (NB) are abundantly supplied to the oxidation (TiO<sub>2</sub>), and reduction sites (Pt), respectively (reasonable delivery effect) facilitating a combined redox reaction. GC-MS chromatograms recorded at different reaction times of the photocatalytic conversion of nitrobenzene in ethanol are



**Figure 3.** Time-dependent change in the concentrations of substrate and products during photoirradiation of nitrobenzene in neat EtOH with a) TiO<sub>2</sub> and b) Pt-TiO<sub>2</sub> catalyst. Reaction conditions: 25 mM of nitrobenzene in ethanol, Catalyst suspended: 50 mg.



**Figure 4.** GC-MS chromatograms at different reaction times for the photocatalytic conversion of nitrobenzene.

presented in Figure 4. These chromatograms reveal the formation of nitrosobenzene, aniline, *N*-hydroxyaniline, 4-anilino-2-methyl-1,2,3,4-tetrahydroquinoline as intermediates.

Earlier it was reported that the irradiation of nitrobenzene (2 mmol) and TiO<sub>2</sub> (0.5 g) in nitrogen-saturated ethanol solution for 8–12 h gave ethoxytetrahydroquinolines as the major product. We obtained 2-methylquinoline with continues purging of nitrogen for 6 h irradiation. Our results reveal that the oxidation power of TiO<sub>2</sub> is well controlled under these experimental conditions.

Analysis of the effect of catalyst concentration revealed that the percentage conversion of nitrobenzene increased from 49 to 70% with increasing amount of Pt-TiO<sub>2</sub> from 0.5 to 1 g L<sup>-1</sup>. As the conversion efficiency decreases above 1 g L<sup>-1</sup>, the optimum catalyst concentration is 1 g L<sup>-1</sup>. The decrease in efficiency at concentrations above 1 g L<sup>-1</sup> may be due to the light scattering by the catalyst particles. It is also found that the increase of substrate concentration from 15 to 65 mM decreases the formation of 2-methylquinoline from 80 to 42% in this reaction.

**Table 1.** Photocatalytic Synthesis of Various Substituted 2-Methylquinolines<sup>a)</sup>

| Run | Reactants                | Product (Yield/%)                                            | By-product /% | Conversion /% |
|-----|--------------------------|--------------------------------------------------------------|---------------|---------------|
| 1   | Nitrobenzene             | 2-Methylquinoline (70)<br>Aniline (23)                       | 6             | 99            |
| 2   | 3-Methylnitrobenzene     | 2,7-Dimethylquinoline (76)<br><i>m</i> -Toluidine (14)       | 9             | 99            |
| 3   | 4-Methylnitrobenzene     | 2,6-Dimethylquinoline (71)<br><i>p</i> -Toluidine (19)       | 8             | 98            |
| 4   | 4-Methoxynitrobenzene    | 6-Methoxy-2-methylquinoline (68)<br><i>p</i> -Anisidine (11) | 7             | 86            |
| 5   | 3,5-Dimethylnitrobenzene | 2,5,7-Trimethylquinoline (68)<br>3,5-Dimethylaniline (16)    | 3             | 87            |
| 6   | 4-Chloronitrobenzene     | 6-Chloro-2-methylquinoline (30)<br>4-Chloroaniline (19)      | 50            | 99            |
| 7   | 4-Fluoronitrobenzene     | 6-Fluoro-2-methylquinoline (16)<br>4-Fluoroaniline (14)      | 69            | 99            |

a) All reactions were performed with a 25 mM alcoholic solution of a reactant 50 mg of Pt-TiO<sub>2</sub> suspension,  $I = 1.381 \times 10^{-6}$  einstein L<sup>-1</sup> s<sup>-1</sup>, irradiation time = 5 h.

This process is facile for the synthesis of various substituted 2-methylquinolines. Photoirradiation of alcohol solutions that contained various substituted nitrobenzenes and the Pt-TiO<sub>2</sub> catalyst successfully afforded the corresponding 2-methylquinolines (Table 1). 3-Methylnitrobenzene and 4-methylnitrobenzene gave 2,7-dimethylquinoline (76%) and 2,6-dimethylquinoline (71%) respectively. 2-Methylquinoline yield for 3-methylnitrobenzene is higher than for 4-methylnitrobenzene. In the synthesis of 2-methylquinoline, reduction of nitro is followed by condensation with aldehyde and cyclization. It seems that the electron-donating group at *p*-position inhibits the condensation of amino group with aldehyde. This is also revealed by the formation of only 68% 6-Methoxy-2-methylquinoline from 4-methoxynitrobenzene which has a strong electron-donating group at *p*-position. In the case of 3,5-dimethylnitrobenzene, the cyclization reaction is hindered due to steric effect and this decreases the product yield (68%) when compared to 3-methylnitrobenzene (76%). In the case of 4-chloro- and 4-fluoronitrobenzenes, the yield of product was very low. This is attributable to photoinduced dehalogenation. Dehalogenated anilines have been identified in GC-MS analysis.

**Mechanism.** Scheme 1 provides a tentative overview of plausible reaction mechanisms leading to the cyclization products identified by GC-MS. The initial steps in the reaction which are necessary for all the reactions are the photocatalytic reduction of nitroaromatic compound and oxidation of the alcohol. The nitroaromatic compound is reduced to aniline by photogenerated conduction band electron on the semiconductor surface. Simultaneously the alcohol is oxidized to the corresponding aldehyde consuming the photogenerated valance band holes on TiO<sub>2</sub>. The photocatalytic formation of an aldehyde from alcohol was well established.<sup>25</sup>

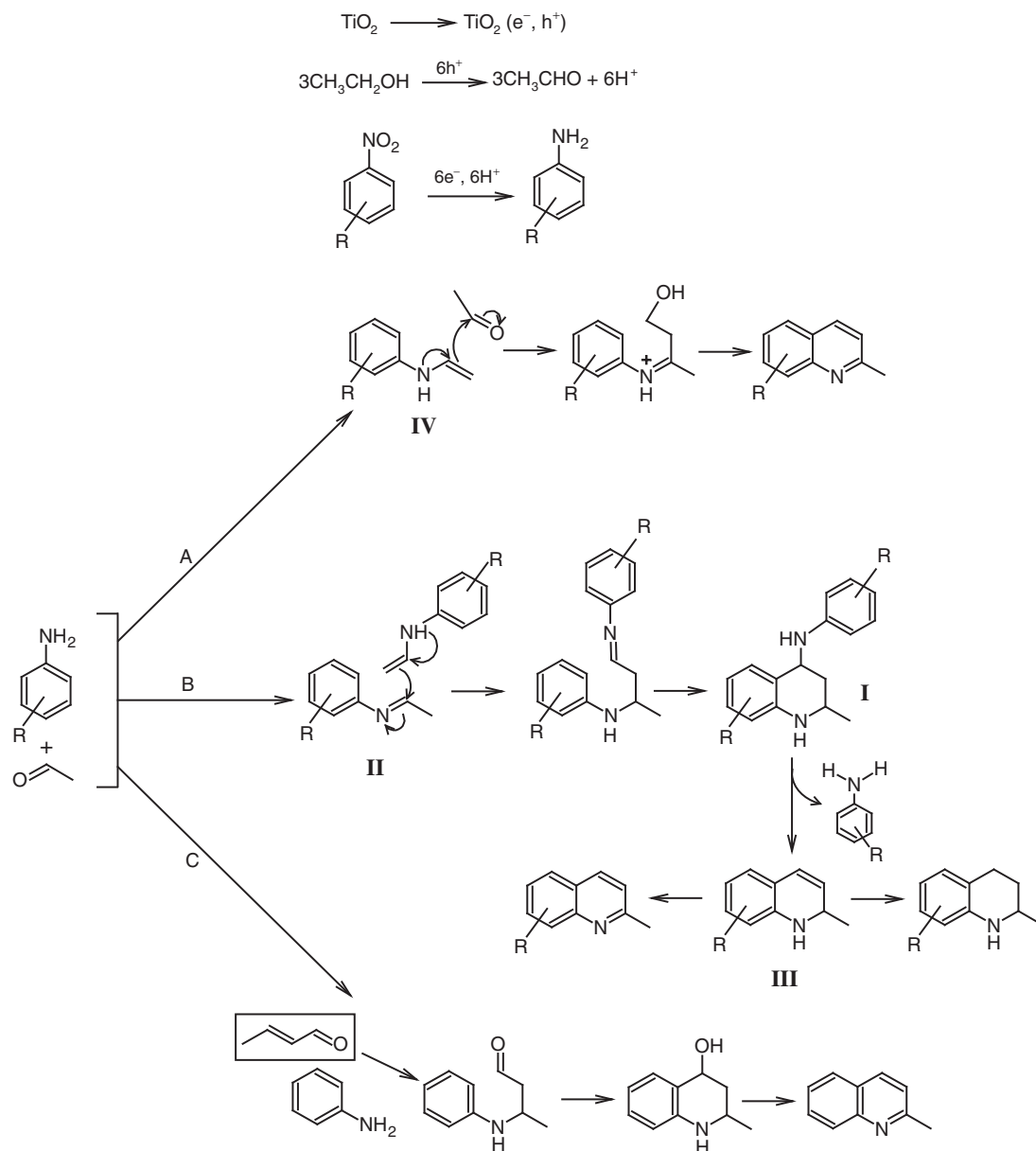
Pathways A and B (Scheme 1) suggest the formation of an imine (Schiff base) via the reaction between the aniline and acetaldehyde, whereas pathway C requires the formation of crotonaldehyde, the product of an aldol condensation of two acetaldehyde units. These pathways are proposed on the basis

of an earlier report on the conversion of nitroarene to tetrahydroquinoline using TiO<sub>2</sub> with a cocatalyst *p*-toluenesulfonic acid.<sup>21</sup> In pathway C, crotonaldehyde is produced in low concentration and consumed readily. It could not be detected by GC-MS under the experimental conditions of this work. In fact, when crotonaldehyde was made to react with *N*-ethylidenaniline thermally, the reaction was completed within 4 h. In the reaction pathway B, the formation of tetrahydroquinoline was also detected by GC-MS (Figure 4). 4-Anilino-2-methyl-1,2,3,4-tetrahydroquinoline (**I**) can be formed via cycloaddition of the imine (**II**) to its enamine tautomer. Subsequent elimination of an aniline molecule from **I** yields the dihydroquinoline (**III**) as intermediate, which on dehydration gives 2-methylquinoline. In the reaction pathway A, titanium enolate formed on the surface of TiO<sub>2</sub> condenses with the aniline to give **IV**, which on further condensation and oxidation yield corresponding 2-methylquinolines. Formation of enolate with TiO<sub>2</sub> was reported by Chen et al.<sup>26</sup>

Photocatalytic experiments in different mixtures of EtOH-H<sub>2</sub>O have also been carried out. Table 2 shows that the yield of 2-methylquinoline from nitrobenzene after 5 h irradiation decreases from 70 to 6% with the increase in amount of water. In water the photogenerated OH radicals can attack nitrobenzene in a nonselective manner. There is a possibility that water favors the hydration of the accumulated aldehyde leading to the corresponding acid and the water can react with imine intermediate.

### Conclusion

In conclusion, Pt-TiO<sub>2</sub> enables efficient 2-methylquinoline production under photoirradiation conditions. This process has significant advantages when compared with other methods: i) a cheap and stable reactant (alcohol), ii) it does not require the use of acids or reductants, and iii) the reaction proceeds under milder ambient conditions. Therefore, this process has the potential to enable a more sustainable 2-methylquinoline synthesis. The combined redox reaction presented here may help to develop a new strategy toward the development of photocatalysis-based organic synthesis.



**Scheme 1.** Schematic overview over the possible reaction pathways for nitrobenzene.

**Table 2.** Effect of Water Content on Photocatalytic Synthesis of 2-Methylquinoline from Nitrobenzene

| Run | Conditions <sup>a)</sup>        | Yield of 2-methylquinoline/% | Conversion /% |
|-----|---------------------------------|------------------------------|---------------|
| 1   | Neat ethanol                    | 70                           | 99            |
| 2   | Ethanol–H <sub>2</sub> O (99/1) | 28                           | 99            |
| 3   | Ethanol–H <sub>2</sub> O (98/2) | 19                           | 99            |
| 4   | Ethanol–H <sub>2</sub> O (96/4) | 6                            | 85            |

a) Condition same as in Table 1.

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### Supporting Information

Catalyst characterization figures such as XRD patterns (Figure S1), AFM images (Figure S2), BET isotherm (Figure S3), DRS (Figure S4), and Tauc plot (Figure S5) are given. This material is available free of charge on the web at <http://www.csj.jp/journals/bcsj/>.

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