



ORIGINAL ARTICLE

Photocatalytic synthesis of 2-methylquinolines with TiO₂ Wackherr and Home Prepared TiO₂ – A comparative study



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Abstract A comparative study was carried out on the efficiency of titanium dioxide specimens Wackherr TiO₂, prepared TiO₂ and Aeroxide P25 toward the photocatalytic synthesis of pharmaceutically important 2-methylquinolines. TiO₂ Wackherr induced significantly faster conversion of nitrobenzene to 2-methylquinoline than Aeroxide P25 when high photocatalyst loadings and high substrate concentrations were used. Photocatalytic synthesis of 2-methylquinolines from substituted nitrobenzenes and anilines show that the product yield is not significantly influenced by the substituents. Low cost TiO₂ Wackherr is more useful when high photocatalyst loading is required at high substrate concentration.

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1. Introduction

Since the first report on the photolysis of water using TiO₂ by Fujishima and Honda (Fujishima and Honda, 1972), photocatalysis by TiO₂ has been widely accepted and exploited as an efficient technology for environmental remediation (Maness et al., 1999; Thomson et al., 2004; Einaga et al., 2002; Hongmin et al., 2005). Titanium dioxide (TiO₂) has been regarded as a benchmark photocatalyst because of its performance, low cost, nontoxicity, stability, and easy availability.

Nowadays notable progress has been made in the applications of semiconductor oxides as catalysts in organic synthesis (Palmisano et al., 2010; Shiraishi and Hirai, 2008). Aeroxide (Degussa P25). (80% anatase; 20% rutile) is a well known and widely investigated photocatalyst (Hoffmann et al., 1995). Since most of the works were carried out with the Aeroxide P25, the present work was focused on a locally available cheap cosmetic pigment TiO₂ Wackherr. More recently, Vione et al., studied the degradation of phenol and benzoic acid in the presence of sunlight using TiO₂ Wackherr's "Oxyde de titane standard" and reported that TiO₂ Wackherr showed a better photocatalytic activity over Degussa P25 in degrading phenol and benzoic acid (Vione et al., 2005).

Quinoline and its derivatives have pharmacological and biochemical significance (Maguire et al., 1994). Hence, great efforts have been made to develop efficient synthetic routes to quinoline derivatives in both synthetic organic and medicinal chemistry. Synthetic methods such as Skraup, Doebner-Von Miller, Friedlander, Combes reactions have been developed for the preparation of quinolines (Skraup, 1880; Doebner

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and Miller, 1883; Friedlander, 1882). But many of these methods are not fully satisfactory with regard to operational simplicity, cost of the reagent and isolated yield. Photocatalytic synthesis of quinoline derivatives from nitrobenzenes using TiO₂, metal doped TiO₂ and other catalysts had been reported (Park et al., 1995; Hakki et al., 2009; Selvam and Swaminathan, 2010, 2011) but not with TiO₂ Wackherr. Hence in this work we aimed toward using this inexpensive TiO₂ Wackherr for the synthesis of 2-methylquinolines (quinaldines) from nitrobenzenes and anilines. An attempt has also been made to identify the reaction intermediates formed during the process, using GC–MS analysis.

2. Experimental

2.1. Materials and methods

All chemicals were of the highest purity available and were used as received without further purification. Nano TiO₂ was prepared by the hydrolysis of titanium tetraisopropoxide (Himedia 98.0%), in isopropanol solution by the addition of distilled water (isopropanol/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 1 h. Metal doped TiO₂ catalyst was prepared by the photoreduction of metal ions on the TiO₂ as per the procedure reported in our previous paper (Selvam and Swaminathan, 2010). pH of the TiO₂ suspension was adjusted to three using perchloric acid. Appropriate amount of metal chloride or nitrate solution was added to the suspension to get the atomic percentage of metal by weight. The mixture was irradiated with UV-light using 4 mercury lamps of 8 W each for 3 h with continuous air supply. Then suspension was filtered, washed and dried at room temperature to obtain metal doped TiO₂ catalyst.

TiO₂ P25 (Aeroxide P25) was a gift from Evonik Degussa corporation, while Oxyde de titane standard was a gift from Wackherr (Sensient Cosmetic Technologies, F-95310 France; BET area ca. 8.5 m² g⁻¹, 100% anatase). Wackherr catalyst has some properties quite similar to the TiO₂ Merck often referred to in the literature.

2.2. Apparatus

X-ray diffraction (XRD) patterns of TiO₂ samples were obtained using a Model D/Max 2550 V 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 DRS of all the catalysts were recorded in Shimadzu UV 2450 model UV–visible spectrophotometer. The morphol-

ogy of catalyst was examined using a JEOL JSM-6701F cold field emission scanning electron microscope (FE-SEM). Samples were mounted on a gold platform placed in the scanning electron microscope for taking images at various magnifications. Scanning electron microscopic (SEM) images were taken on gold-coated samples using a JEOL apparatus model JSM-5610LV, equipped with INCA EDX probe for the energy dispersive X-ray microanalysis (EDS). 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 the analysis was performed at 77 K with N₂ gas as the adsorbate. The Brunauer–Emmett–Teller (BET) multi-point method least-square fit provided the specific surface area.

2.3. Photocatalytic synthesis of quinaldines

In a typical experimental run, 50 mg of TiO₂ catalyst was suspended in 25 mL of an absolute ethanolic solution containing 25 mM of the nitrobenzenes or anilines and irradiated by a 365 nm medium-pressure mercury lamp (Sankyo Denki, Japan) after purging with N₂ for 30 min. The intensity of irradiation entering the glass tube was measured by potassium ferrioxalate actinometry method. The actinometer solution was irradiated under conditions similar to those used for photoreaction. Light intensity (I_0) of four lamps measured using 50 mL of the actinometer solution was 1.381×10^{-6} einstein L⁻¹ s⁻¹. N₂ bubbling (flow rate = 6.1 mL s⁻¹) 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

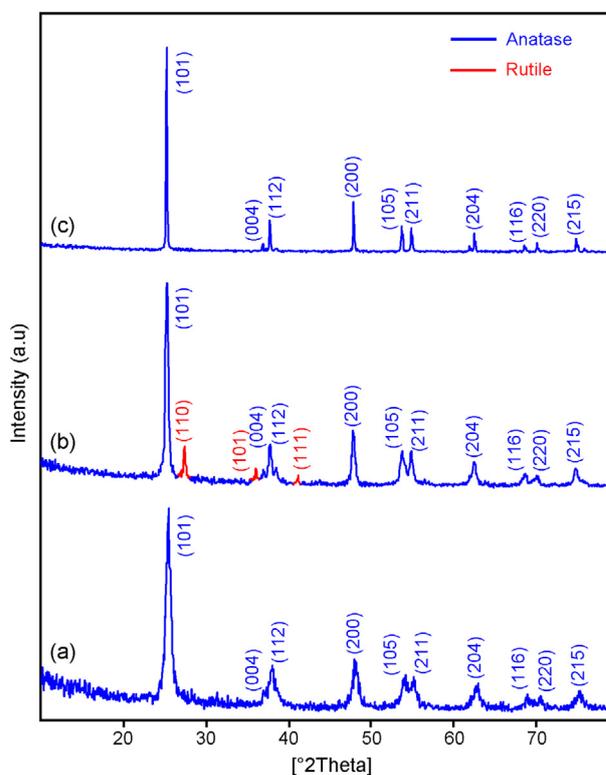


Figure 1 XRD patterns from (a) Prepared TiO₂, (b) TiO₂–P25 Degussa and (c) TiO₂ Wackherr.

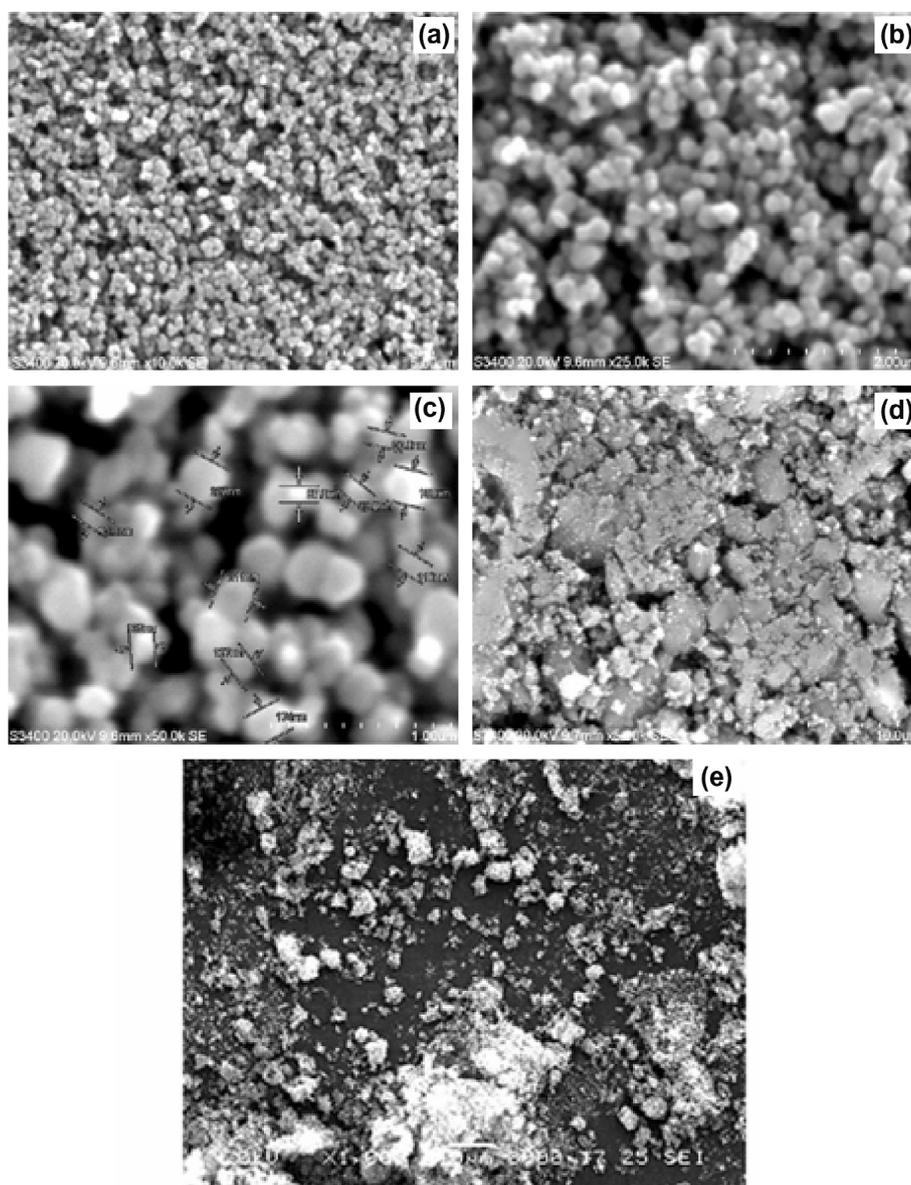


Figure 2 SEM images of (a–c) TiO_2 Wackherr, (d) prepared TiO_2 and (e) TiO_2 -P25 Degussa.

detector was used. GC/MS analysis was carried out using Varian 2000 Thermo and the detail of instrument is described in our earlier paper (Muthu et al., 2009). The isolation of product was performed by column chromatography on a silica gel column by eluting with a co-solvent of hexane and ethyl acetate (volume ratio 8:2).

3. Results and discussion

3.1. Characterization of the catalysts

3.1.1. XRD analysis

X-ray diffraction (XRD) patterns of prepared TiO_2 , TiO_2 -P25 Degussa and TiO_2 Wackherr are shown in Fig. 1(a–c). The XRD patterns of prepared TiO_2 and TiO_2 Wackherr (Fig. 1a and c) are identical with the standard pattern of anatase (JCPDS 01-078-2486C), and the rutile lines (01-089-0553C) 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_2 , respectively. This clearly reveals that the prepared TiO_2 and TiO_2 Wackherr are of anatase phase. Fig. 1b displays the XRD pattern of TiO_2 -P25. Since it is a mixture of 80% anatase and 20% rutile, XRD pattern shows both anatase and rutile lines. The peaks obtained for Wackherr are narrow. This implies a good crystalline structure in TiO_2 Wackherr when compared to TiO_2 -P25 and prepared TiO_2 . The average crystalline grain size of TiO_2 Wackherr, determined using Debye–Scherrer formula, was found to be 160 nm.

3.1.2. Surface area analysis

BET surface area analysis reveals that TiO_2 Wackherr has a surface area of $8.5 \text{ m}^2 \text{ g}^{-1}$ which is less than those of Aeroxide P25 ($50 \text{ m}^2 \text{ g}^{-1}$) and prepared TiO_2 ($86.5 \text{ m}^2 \text{ g}^{-1}$). Since the sizes of the TiO_2 Wackherr are higher than other catalysts, its surface area is less.

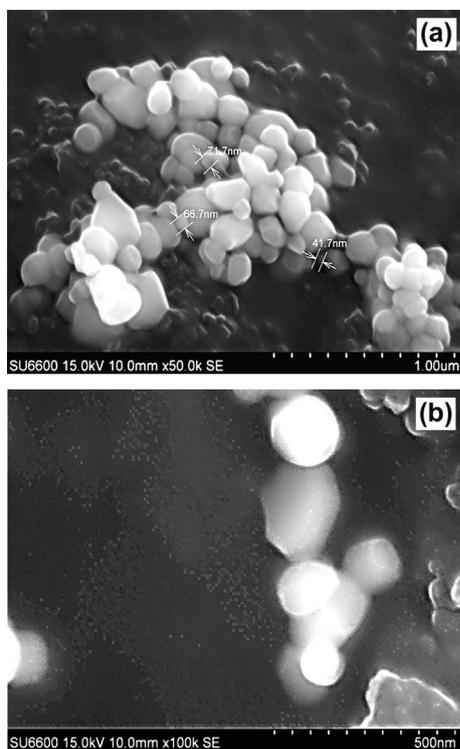


Figure 3 FE-SEM images of TiO₂ Wackherr (a) 50 k and (b) 100 k.

3.1.3. Scanning electron microscope analysis

SEM images of TiO₂ Wackherr (Fig. 2a–c) and prepared TiO₂ (2d) and TiO₂-P25 (2e) are shown in Fig. 2. It can be seen that the TiO₂ Wackherr particles are quite uniform and monodispersed, with an average diameter of about 100 nm (Fig. 2c). The SEM image of prepared TiO₂ (Fig. 2d) depicts that the particles are in the form of aggregates and the surface of the prepared TiO₂ is irregular and not spherical as TiO₂ wackherr. In the case of TiO₂-P25, the size of the particles is non-uniform and crystallinity is also low when compared to TiO₂ Wackherr. Field emission scanning electron microscopy (FE-SEM) images were taken to obtain detailed information about the microstructure and morphology of the Wackherr samples. Fig. 3(a and b) show the low and high-magnification FE-SEM images of TiO₂ Wackherr microspheres. The particles have ball-shaped microcrystal structures with diameters in the range of 50–300 nm. From the pictures, it is also found that some small round particles, having a diameter of about 50 nm are adhering microspheres.

3.1.4. UV-Visible diffuse reflectance spectra

The diffuse reflectance spectra of TiO₂ Wackherr and prepared TiO₂ catalyst are displayed in Fig. 4. TiO₂ Wackherr (Fig. 4b) has slightly higher absorption in the UV region than prepared TiO₂ (Fig. 4a). The band gap energy (E_g) of TiO₂ Wackherr, determined using the equation $E_g = 1239.8/\lambda$, where λ is the wavelength of the absorption edge in the spectrum is 3.12 eV, which is equivalent to the wavelength of 397 nm.

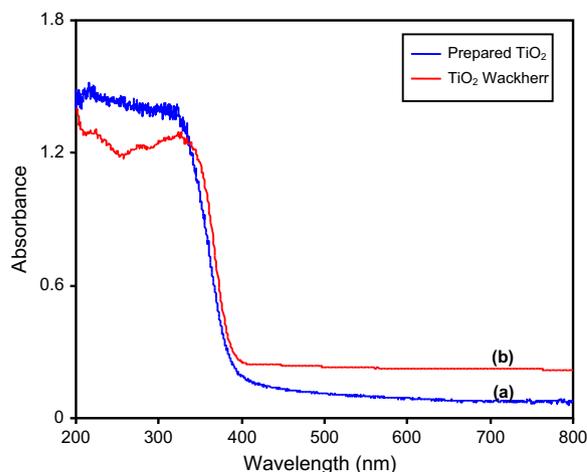


Figure 4 Diffuse reflectance spectra of (a) prepared TiO₂ and (b) TiO₂ Wackherr.

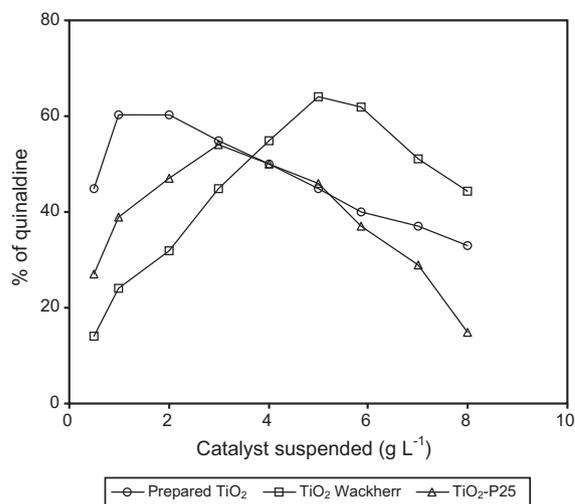


Figure 5 Comparison of effect of catalyst amount for the conversion of nitrobenzene to quinaldine. [Nitrobenzene] = 25 mM, N₂ flow rate = 6.1 mL s⁻¹, $I_{UV} = 1.381 \times 10^{-6}$ einstein L⁻¹ s⁻¹, irradiation time = 5 h.

3.2. Photocatalytic activity

3.2.1. Comparison of catalytic efficiencies

The photocatalytic conversion of nitrobenzene to 2-methylquinoline in absolute ethanol with continuous purging of N₂ was studied as a function of catalyst loading for three photocatalysts and the results are shown in Fig. 5. With prepared TiO₂, 2-methylquinoline formation reaches a maximum value at 1 g L⁻¹, while in the case of the TiO₂-P25 formation of 2-methylquinoline is maximum at 3 g L⁻¹. But TiO₂ Wackherr shows an increasing 2-methylquinoline formation up to 5 g L⁻¹. Although prepared TiO₂ and TiO₂-P25 are more active at low photocatalyst loading, TiO₂ Wackherr is active at high loading of 5 g L⁻¹. According to the earlier report (Vione et al., 2005), TiO₂ Wackherr has less light scattering property when compared to the other forms of TiO₂. This is the reason for its increased activity at high loading.

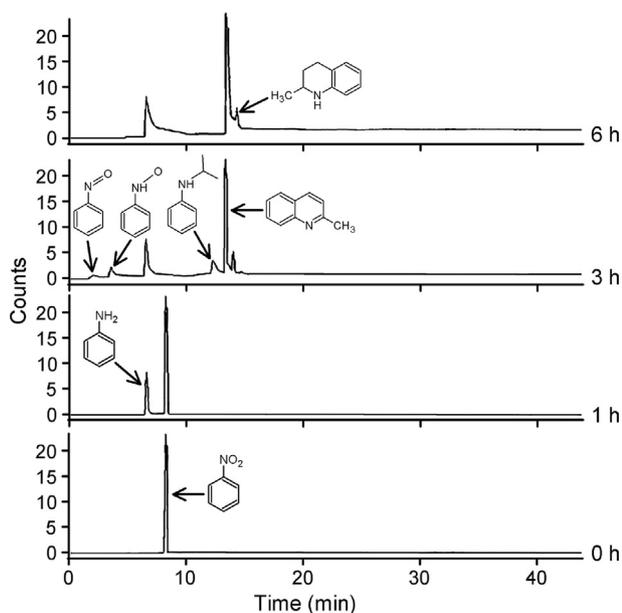


Figure 6 GC-MS chromatograms at different reaction times for the photocatalytic conversion of nitrobenzene.

TiO₂ Wackherr is more photoactive (64% product yield) than Aeroxide P25 (54%) and prepared TiO₂ (60%), in spite of its lower surface area. This behavior can be attributed to lower scattering of UV radiation by TiO₂ Wackherr. Control experiments demonstrated that nitrobenzene did not undergo any reaction in the absence of TiO₂ or without irradiation. GC-MS chromatograms recorded at different reaction times of the photocatalytic conversion of nitrobenzene in ethanol (Fig. 6) reveal the formation of nitrosobenzene, aniline, *N*-hydroxyaniline, *N*-(propan-2-yl)aniline, 2-Methyl-1,2,3,4-

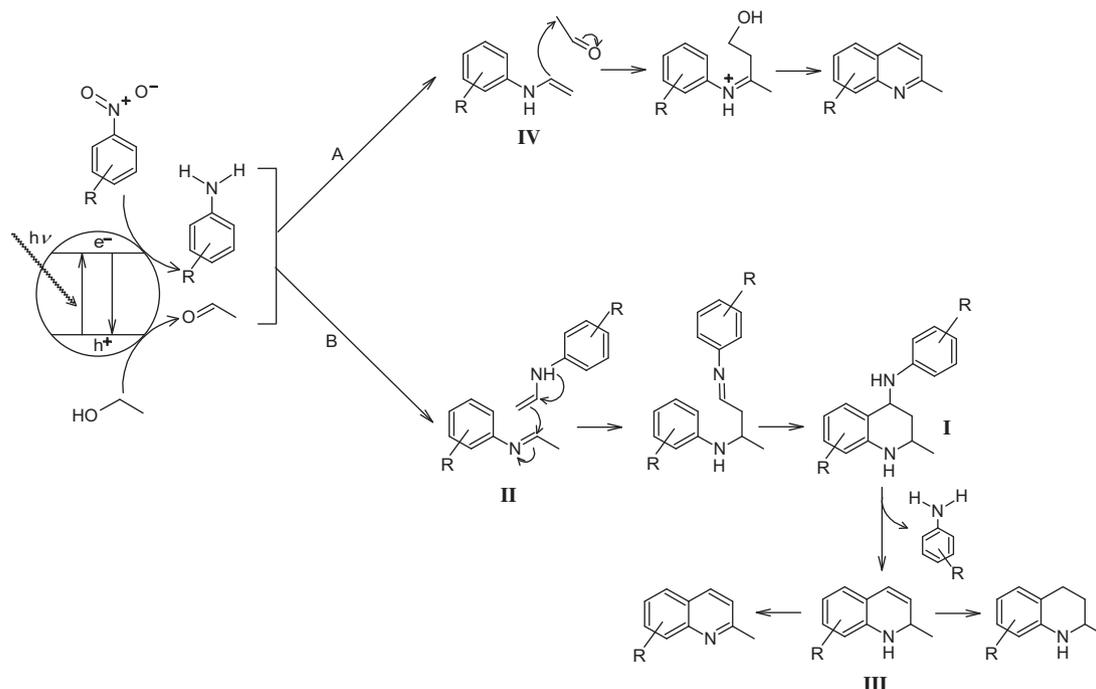
tetrahydroquinolin-4-yl(phenyl)amine as intermediates during the 2-methylquinoline formation. The formation of byproducts aniline and 2-Methyl-1,2,3,4-tetrahydroquinoline is indicated by GC-MS chromatogram obtained after 6 h. Since the intermediates formed are same as those formed in Au-TiO₂ catalyzed 2-methylquinoline synthesis from nitrobenzene, the mechanism reported for Au-TiO₂ holds good for this reaction also (Selvam and Swaminathan, 2010). According to this mechanism, initially alcohol is oxidized to the corresponding aldehyde consuming the photogenerated valence band holes on TiO₂ Wackherr. The oxidized product of ethanol condensed with aniline produces an imine (Schiff base) which on further condensation and cyclization yields corresponding quinaldine (Scheme 1). These pathways are proposed on the basis of earlier report on the conversion of nitroarene to tetrahydroquinoline using TiO₂ with a co-catalyst *p*-toluene sulfonic acid (Hakki et al., 2009).

3.2.2. Influence of the substrate concentration

The effect of the initial nitrobenzene concentration on 2-methylquinoline synthesis using TiO₂ Wackherr was investigated and the results are compared with prepared TiO₂ (Table 1). It is found that the increase in the substrate concentration decreases the percentage of product formation. It should be pointed out that even at high initial concentration of nitrobenzene (45 mM) about 45% product formation could be achieved in 5 h whereas prepared TiO₂ gave only 29% product at 45 mM substrate concentration. This indicates that TiO₂ Wackherr catalyst can also work well at a high initial concentration of nitrobenzene.

3.2.3. Effect of metal doping

In recent years, particular emphasis is placed on the use of metal doped nano-sized semiconductor oxides as they show product selectivity and visible light activity (Tada et al.,



Scheme 1 Schematic overview over the possible reaction pathways.

Table 1 Effect of [nitrobenzene] on the photocatalytic cyclization with TiO₂ Wackherr.

Concentration of nitrobenzene (mM)	Prepared TiO ₂ (%)	TiO ₂ Wackherr (%)
15	55	89
25	44	64
35	38	54
45	29	45

TiO₂ Wackherr = 5 g L⁻¹, prepared TiO₂ = 1 g L⁻¹, N₂ flow rate = 6.1 mL s⁻¹, I_{UV} = 1.381 × 10⁻⁶ einstein L⁻¹ s⁻¹, irradiation time = 5 h.

Table 2 Effect metal doping on the photocatalytic cyclization with TiO₂ Wackherr.

S. no.	Catalyst	Conversion (%)
1	Bare TiO ₂ Wackherr	64
2	1.5% Ag doped TiO ₂ Wackherr	58
3	1.0% Au doped TiO ₂ Wackherr	49
4	1.5% Pt doped TiO ₂ Wackherr	43

Catalyst suspended = 5 g L⁻¹, N₂ flow rate = 6.1 mL s⁻¹, I_{UV} = 1.381 × 10⁻⁶ einstein L⁻¹ s⁻¹, irradiation time = 5 h.

1998; Pal et al., 2007). Ag, Au and Pt doped TiO₂ Wackherr were prepared and experiments with these doped catalysts under identical conditions were carried out for the conversion of nitrobenzene to 2-methylquinoline. The results (Table 2) reveal that the photocatalytic efficiencies of metal doped TiO₂ Wackherr catalysts are lower when compared to the bare TiO₂ Wackherr. This shows that metal doping is not effective in TiO₂ Wackherr. Since the metal doping was found to be effective in nanophotocatalysts (Selvam and Swaminathan, 2010, 2011), larger particle size of TiO₂ Wackherr (50–300 nm) might have affected the activity of the metal doped catalysts.

3.2.4. Effect of substituents

To demonstrate the generality and scope of this method, we examined this reaction with different nitrobenzenes in ethanol using TiO₂ Wackherr catalyst under UV light and the results are summarized in Table 3. Photoirradiation of alcohol solutions of different nitrobenzenes with TiO₂ Wackherr catalyst successfully afforded the corresponding 2-methylquinolines. There is no significant effect of substituents on the product yield. 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.

Table 3 Photocatalytic synthesis of various substituted quinaldines from nitrobenzenes using TiO₂ Wackherr.

Run	Reactant	Product yield (%)	Byproduct (%)	Conversion (%)
1	Nitrobenzene	Quinaldine (64)	34	98
2	3-Nitrotoluene	2,7-Dimethylquinoline (56)	33	89
3	4-Nitrotoluene	2,6-Dimethylquinoline (57)	41	98
4	4-Methoxynitrobenzene	6-Methoxy-2-methylquinoline (58)	36	94
5	3,5-Dimethylnitrobenzene	2,5,7-Trimethylquinoline (61)	28	89
6	4-Chloronitrobenzene	6-Chloro-2-methylquinoline (25)	74	99
7	4-Fluoronitrobenzene	6-Fluoro-2-methylquinoline (11)	88	99

All reactions were performed with a 25 mM alcoholic solution of reactant, catalyst suspended = 5 g L⁻¹, N₂ flow rate = 6.1 mL s⁻¹, I_{UV} = 1.381 × 10⁻⁶ einstein L⁻¹ s⁻¹, irradiation time = 5 h.

Table 4 Photocatalytic synthesis of various substituted quinaldines from anilines using TiO₂ Wackherr.

Run	Reactant	Product yield (%)	Byproduct (%)	Conversion (%)
1	Aniline	Quinaldine (64)	25	89
2	<i>o</i> -Toluidine	2,8-Dimethylquinoline (61)	22	83
3	<i>m</i> -Toluidine	2,7-Dimethylquinoline (64)	25	89
4	<i>p</i> -Toluidine	2,6-Dimethylquinoline (70)	14	84
4	<i>o</i> -Anisidine	5-Methoxy-2-methylquinoline (62)	19	81
5	<i>m</i> -Anisidine	7-Methoxy-2-methylquinoline (68)	23	91
6	<i>p</i> -Anisidine	6-Methoxy-2-methylquinoline (70)	19	89
7	3,5-Dimethylaniline	2,5,7-Trimethylquinoline (69)	25	94
8	2,5-Dimethylaniline	2,5,8-Trimethylquinoline (50)	17	67
9	3,5-Dimethoxyaniline	5,7-Dimethoxy-2-methylquinoline (69)	24	93
10	<i>p</i> -Phenatidine	6-Ethoxyquinaldine (72)	20	92
11	<i>p</i> -Chloroaniline	6-Chloro-2-methylquinoline (19)	80	99
12	<i>p</i> -Fluoroaniline	6-Fluoro-2-methylquinoline (14)	83	97

All reactions were performed with a 25 mM alcoholic solution of reactant, catalyst suspended = 5 g L⁻¹, N₂ flow rate = 6.1 mL s⁻¹, I_{UV} = 1.381 × 10⁻⁶ einstein L⁻¹ s⁻¹, irradiation time = 5 h.

3.2.5. Photocatalytic synthesis of quinaldines from anilines using TiO₂ Wackherr

As the reaction with nitrobenzene proceeds through aniline, we extended the use of this catalyst for 2-methylquinoline synthesis from anilines. Aniline with neat ethanol gave corresponding 2-methylquinoline in good yield (64%) under UV light. This process is tolerant for the synthesis of 2-methylquinolines from various substituted anilines (Table 4). The percentages of 2-methylquinolines formation from substituted anilines are higher than the percentages of 2-methylquinolines formation from substituted nitrobenzenes with TiO₂ Wackherr.

Under optimum catalyst loading TiO₂ Wackherr is more efficient than both TiO₂-P25 and prepared TiO₂ in UV light. It is found from FE-SEM that TiO₂ Wackherr has a larger particle size when compared to prepared TiO₂ and TiO₂-P25. Larger size of the particle results in more favorable optical properties due to lower scattering in UV region and as a consequence shows better performance at high catalyst loading.

4. Conclusions

We have developed an economical and efficient method for the synthesis of 2-methylquinoline from nitrobenzenes or anilines with neat ethanol using a cheap TiO₂ Wackherr. Despite lower surface area, TiO₂ Wackherr is more photoactive (64% product yield) than Aeroxide P25 (54%) and prepared TiO₂ (60%) at higher loading. This behavior can be attributed to lower scattering of UV radiation by TiO₂ Wackherr. This paper describes the first observation of TiO₂ Wackherr catalyzed synthesis of 2-methylquinoline. Since TiO₂ Wackherr is more efficient and cheaper than the prepared TiO₂ and TiO₂-P25, it can be used for the large scale preparation of 2-methylquinoline.

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