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Photocatalytic reaction of arylamines/alcohols on TiO_2 nano-particles

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Abstract In this article, the photocatalytic reaction of aniline and 4-amino *N*,*N*-dimethyl aniline with methanol, ethanol and isopropanol on anatase TiO_2 nano-particles under UV (365-nm wavelength) irradiation was examined. The concentration of unreacted arylamines and products was measured by gas chromatography picks integration, and then the products were identified by mass spectroscopy analysis. By making a comparison within the rates of photocatalysis of each arylamine in different alcohols under various irradiation times, it was revealed that, in all cases, the sequence of photocatalysis rate was methanol > ethanol > isopropanol. In reactions where the concentrations of arylamine were lower than 10 mmol/l, imines were the main products and the alkylation of amines was not observed. In the higher concentration of arylamines, oxidation and dimerization was occurred.

Keywords Photocatalytic reaction · Arylamine · TiO_2 nano-particle · GC-MS analysis

Introduction

Heterogeneous photocatalysis has been extensively investigated as a possible method for pollutant removal [1–3], organic synthesis [4–6] and bactericidal activity [7]. Nano-sized titania powder is widely used a semiconductor photocatalyst, owing to its non-toxic nature, chemical stability, availability, low cost and capability of easy preparation in the nano-particulate form with high surface area [8].

The initial step in TiO_2-mediated photocatalytic degradation is proposed to involve the generation of an (e^-/p^+) pair, leading mainly to the formation of hydroxyl radicals

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($^{\bullet}OH$), as well as super oxide radical anions ($O_2^{\bullet-}$) and hydroperoxy radicals ($^{\bullet}OOH$). These radicals are oxidizing species in the photocatalytic oxidation processes [9, 10]. Among the above-mentioned radicals from which TiO_2 are produced by photocatalysis, hydroxyl radicals are the most powerful oxidizing species that can attack organic contaminants present at or near the surface of TiO_2 particles [11]. In heterogeneous photocatalysis studies involved with semiconductor powders, thermodynamic and kinetic aspects, the surface area and photocatalyst particle size are important factors for the identification of the reaction product [12].

In recent years, photocatalysis reaction of TiO_2 on arylamines has attracted many researchers due to its wide range of application in the organic dyes industries [12–16]. The mechanism of TiO_2-photocatalysed degradation of aniline derivative in acidic and alkaline mediums has been studied by Canle et al. [12]. They have reported that photocatalytic degradation of arylamines in acidic medium was inhibited due to electrostatic repulsion between the positively charged surface and protonated amines, while in alkaline medium, the main photoproduct of degradation of aniline is nitrobenzene. As an example, in alkaline medium, the degradation of aniline has been investigated using an alkaline aqueous TiO_2 suspension containing carbonate ions [17]. The presence of carbonate in TiO_2 suspension increases the number of active adsorption sites on the TiO_2 particle surface. The major products in this reaction were identified to be azobenzene, *p*-benzoquinone, nitrobenzene and NH_3. Although aniline at the ppm level is mineralised by illuminated TiO_2, at higher concentrations, it is oxidized to azobenzene [13]. *N*-alkylation of amines by photocatalytic reaction in a microreaction system using Pt-free TiO_2 and Pt-loaded TiO_2 has been investigated [18]. It was reported that the *N*-alkylation did not occur by the irradiation of Pt-free TiO_2 in a conventional batch reactor. To make a long story short, there has been a lot of interest in the photocatalytic reaction of arylamines on $TiO_{2,}$, but the results reported in the literature are partly controversial.

In the current work, we have investigated the photocatalytic reaction of two arylamines (aniline and 4-amino *N*,*N*-dimethyl aniline) using TiO_2 nano-powder suspension in alcohols (methanol, ethanol and isopropanol) and the products of photoreaction were followed by GC-MS analysis.

Experimental

Synthesis of photocatalyst

Nano-powder anatase TiO_2 samples were synthesised by the precipitation method and dehydrated with the azeotropic distillation technique, as we reported in previous work [8]. The sizes of nano-powders obtained after calcinations were 15–25 nm and the surface area measured by the BET method was 75–80 m^2/g.

Photocatalytic activity

The arylamines (aniline and 4-amino *N*,*N*-dimethyl aniline) were dissolved separately in methanol, ethanol and isopropanol with 1–10 mmol/L concentrations.

A sample of 20 mg synthesised TiO_2 nano-powder was added to each Pyrex volumetric balloon containing 10 mL of the arylamine solution. The contents of balloons were sonicated in an ultrasound bath for 10 min. The arylamines solutions, in the presence and in the absence of TiO_2, were irradiated for 1–40 h by five UV lamps ($\lambda = 360$ nm) with 40 W power, in an irradiation box.

Analysis

The reaction products were analysed by gas chromatography–mass selective detector (GC-MS) from Agilent Technologies, GC-6890N and MS-5973N model, with the column HP-5, length 30 m, I.D. 0.25 mm and film thickness 0.25 µm. The employed GC condition was: initial temperature 100 °C, hold for 3 min with the ramp rate 8 °C/min and the final temperature was 250 °C. The concentration of unreacted arylamine and products was obtained from the integration of chromatogram picks.

Results and discussions

Arylamines are widely used as raw materials in organic dye industries and are known to be highly toxic chemicals. The two arylamines which were chosen for this experiment are aniline (An) and 4-amino *N*,*N*-dimethyl aniline (ADA).

An amount of 10 mL of ADA solutions in alcohol (methanol, ethanol, isopropanol) with 5 mmol/L concentration and 20 mg TiO_2 nano-powder was sonicated for 10 min, and then irradiated under 40 W UVA. The rate of decrease of the ADA concentration is shown in Fig. 1. As shown in this figure, the rate of photocatalytic degradation of ADA in methanol is higher than ethanol and isopropanol, respectively. After 40 h irradiation in the presence of TiO_2 nano-powder, the ADA had completely disappeared in methanol and ethanol. However, the concentration of ADA in isopropanol reduced slowly and after 24 h, only 20% of the initial concentration was decomposed. To compare the results, a blank experiment was carried out on ADA/ethanol solution in the absence of TiO_2 particles. ADA did not effectively degrade under similar conditions (see Fig. 1).

The chromatogram of photocatalytic reaction products of ADA and methanol is displayed in Fig. 2. The pick at the 8.96 min retention time (RT) corresponds to ADA and the pick at RT = 9.83 min corresponds to the major product. The mass spectra of major product are shown in Fig. 3. All of the picks in the mass spectra are matched with 4(methylene amino) phenyl dimethyl amine (1). The photocatalytic reaction products of ADA/ethanol solution after 30 h irradiation are shown in Fig. 4. This chromatogram shows two major products at RT = 11.01 and RT = 11.68. The mass spectrum of the first product is shown in Fig. 5. This spectrum confirms the formation of 4(ethylene amino) phenyl dimethyl amine (2) and dialkenylation may have occurred in ethanol (RT = 11.68). So, from the obtained results, we can propose the reaction process as shown in Scheme 1 for imines formation.

However, the rate of reaction in isopropanol was lower than the other two alcohols. The chromatogram of this reaction product after 24 h irradiation is shown

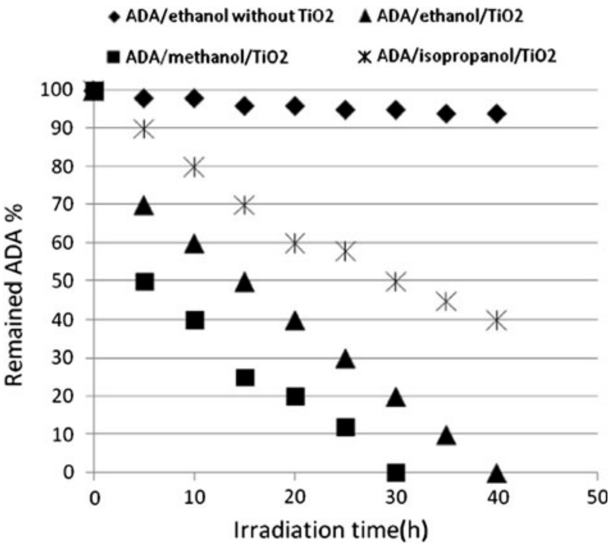
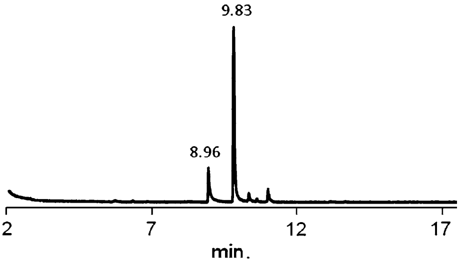


Fig. 1 Variations of ADA concentrations (%) in alcohol as a function of the irradiation time. The samples were 10 mL ADA in alcohol with 5 mmol/L concentration and 20 mg TiO_2

Fig. 2 Chromatogram of photocatalytic reaction product of ADA and methanol after 20 h irradiation. The pick at RT = 8.96 min corresponds to ADA and RT = 9.83 is the main product



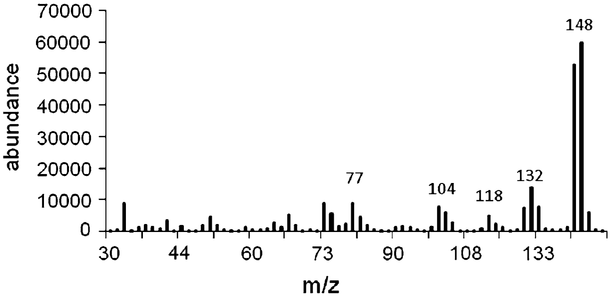


Fig. 3 Mass spectra of the main product of ADA and methanol with TiO_2 (from GC-MS spectroscopy, RT = 9.83). The mass spectra completely matched with 4(methylene amino) phenyl dimethyl amine

in Fig. 6 and the mass spectrum of the major product (RT = 11.71 min) is shown in Fig. 7. The addition of isopropenyl on amine is confirmed by characteristic picks in m/e 176, 161, 145, 120, 105 and 77.

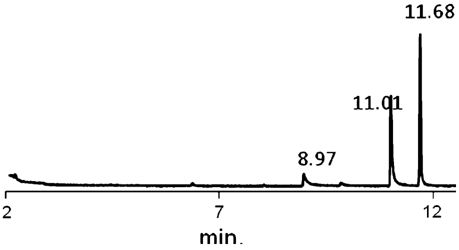


Fig. 4 Chromatogram of photocatalytic reaction product of ADA and ethanol after 30 h irradiation. The pick at RT = 8.96 min corresponds to ADA and RT = 11.01 and 11.68 are the main products

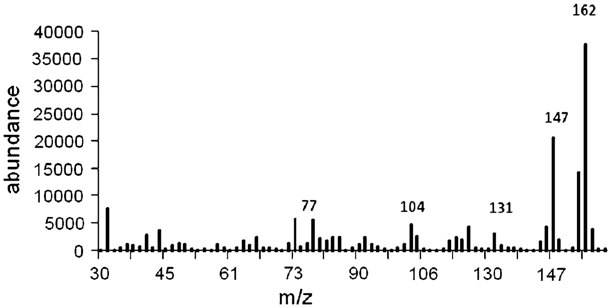
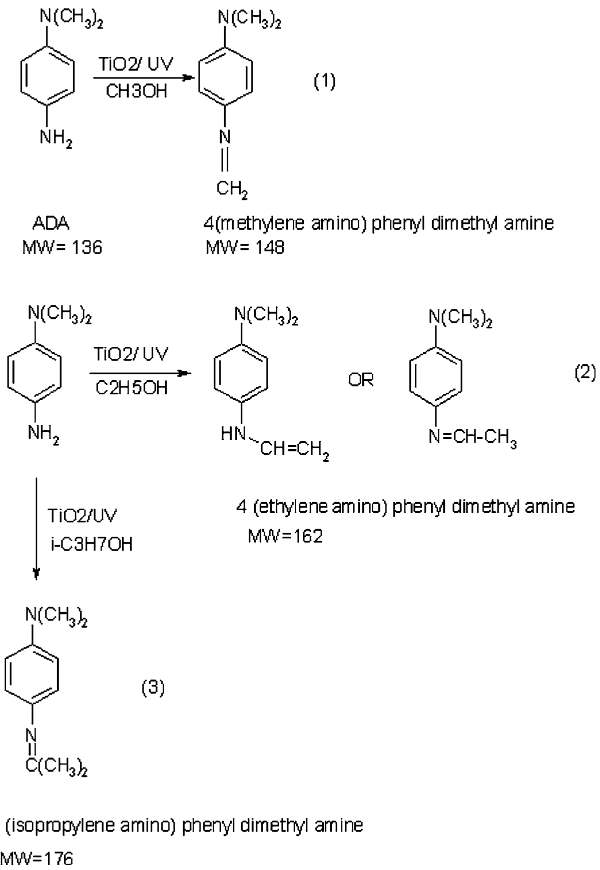


Fig. 5 Mass spectra of the main product of ADA and ethanol with TiO_2 (from GC-MS spectroscopy, RT = 11.01). The mass spectra completely matched with 4(ethylene amino) phenyl dimethyl amine

After a long period of UVA irradiation (about 70 h) in the presence of TiO_2, ADA was completely decomposed in methanol and ethanol. But, during the same time, ADA in isopropanol was converted to various compounds. Although in the photodegradation process, especially at higher concentrations ($\geq$50 mmol), the dimerisation of arylamine with the violet colour may have occurred, at the lower concentrations ($\leq$5 mmol/L), ADA did not dimerize.

The rate of photocatalytic reaction of aniline in alcohol was higher than ADA. Figure 8 shows the decreasing rate of aniline in the 10 mL aniline/alcohol solutions with 1 mmol/L concentration of aniline in the presence and absence of TiO_2. As shown in this figure, aniline remained unchanged in the absence of TiO_2 after 5 h irradiation and, similar to the ADA, photocatalytic reaction of aniline–methanol and aniline–ethanol is more effective than isopropanol. The chromatogram of the photocatalytic reaction of aniline in methanol after 3 h is shown in Fig. 9. During the 3-h reaction time, more than 82.5% of aniline was converted to other compounds. In this chromatogram, the pick at RT = 2.97 corresponds to the aniline and the pick at RT = 2.68 corresponds to the product. The mass spectra of this product match completely with *N*-methylene amino phenyl (the mass spectra are displayed in Fig. 10). During this time, the number of products in ethanol is greater and a small amount of 2-methyl quinoline is considered to be additional to N-ethylene amino phenyl. At the higher concentrations (more than 50 mmol/L), many various products, e.g. azo benzene, azoxy benzene and 4-phenyl azo phenol, were formed. Scheme 2 shows the reaction process of the photocatalytic reaction of aniline in alcohols.



Scheme 1 Alkenylation of ADA in alcohol in the presence of TiO_2 under UV (365 nm) irradiation

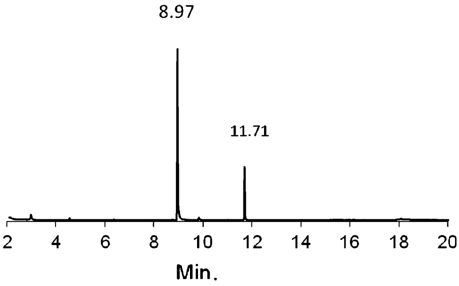


Fig. 6 Chromatogram of photocatalytical reaction product of ADA and isopropanol after 24 h irradiation. The pick at RT = 8.96 min corresponds to ADA and RT = 11.71 is the main product

To investigate the reason for the lower reaction rate of arylamine in isopropanol, the pure isopropanol with TiO_2 nano-powder was irradiated under UVA lamps. As a result, various compounds were produced. The products of reaction were acetone, isopropyl orthoformate and acetaldehyde diisopropyl acetate, as identified by GC-MS analysis. A condensation reaction between amines and ketones or aldehydes (from photocatalytic reaction of alcohols) may have afforded imine or enamine

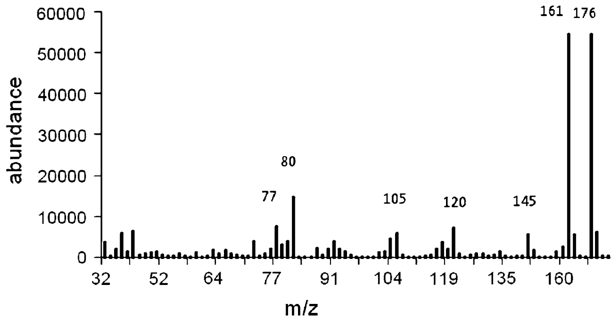


Fig. 7 Mass spectra of the main product of ADA and isopropanol with TiO_2 (from GC-MS spectroscopy, RT = 11.71). The mass spectra completely matched with 4(isopropylene amino) phenyl dimethyl amine

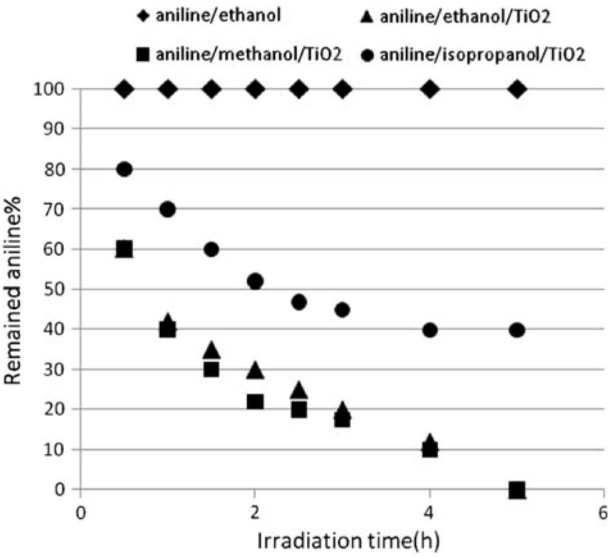
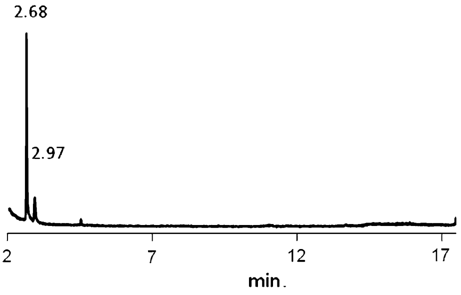


Fig. 8 Variations of aniline concentrations (%) in alcohol as a function of the irradiation time. The samples were 10 mL aniline in alcohol with 1 mmol/L concentration and 20 mg TiO_2

Fig. 9 Chromatogram of photocatalytic reaction product of aniline and methanol after 3 h irradiation. The pick at RT = 2.97 min corresponds to aniline and RT = 2.68 is the main product



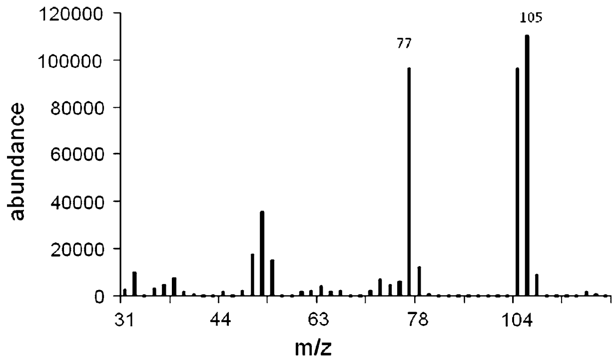
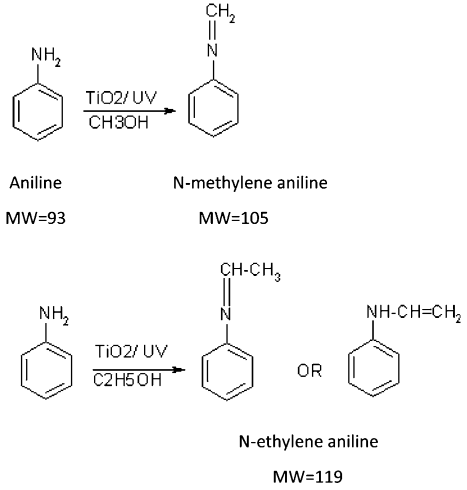


Fig. 10 Mass spectra of the main product of aniline and methanol with TiO_2 (from GC-MS spectroscopy, RT = 2.68). The mass spectra completely matched with *N*-methylene aniline



Scheme 2 Alkenylation of aniline in alcohol in the presence of TiO_2 under UV (365 nm) irradiation

compounds. The photocatalytic reaction of alcohol with longer chains is more complex and leads to the formation of various products. This can be attributed to the formation of numerous radical species which finally react together perfectly.

Conclusions

Samples containing arylamine/alcohol and TiO_2 nano-powder suspensions were irradiated with 40 W UVA lamps. The GC-MS analysis showed the imine formation at the concentrations lower than 10 mmol/L. The imines can be isomerised to enamines form. The sequence of photocatalytic reaction rate was methanol > ethanol > isopropanol. Investigation of these reaction mechanisms showed that active radicals of alcohol forms in the presence of TiO_2 under UVA irradiation and these radicals initiate the reactions. The reason for the difference in the reaction rates correspond to the stability of formed radicals from alcohol. Also, the variety of radicals from isopropanol is more than two other alcohols, so the radicals react together perfectly. At the higher concentrations (more than 10 mmol), oxidation of arylamine occurs and some products, e.g. azobenzene, azoxy benzene, 4-phenyl azo phenol and some of their derivatives, are formed. In the results of these reactions, the alkylation of arylamines is not observed in any of the reaction studies.

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