Catalysis Communications 10 (2009) 989–994

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Practical synthesis of aromatic amines by photocatalytic reduction of aromatic nitro compounds on nanoparticles N-doped TiO_2

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ARTICLE INFO

Article history:
Received 9 September 2008
Received in revised form 15 December 2008
Accepted 17 December 2008
Available online 25 December 2008

Keywords:
Reduction
Aromatic amines
N-doped TiO_2
Potassium iodide

ABSTRACT

A novel efficient method for the catalytic reduction of aromatic nitro compounds to the corresponding amines was reported. Aromatic nitro compounds were chemoselectively reduced to the corresponding amines by using N-doped TiO_2 and potassium iodide as photocatalysts in the presence of methanol. The novel method is highly efficient with very short reaction time (<20 min), excellent yields (>90%) and wide functional group tolerance such as carbonyl, halogen, amino, hydroxyl and carboxylic acid groups. And N-doped TiO_2 was prepared by a modified sol-gel method using urea as nitrogen source and had higher photocatalytic activity comparing with pure TiO_2. The catalysts were characterized by XRD, XPS, TEM and UV–Vis DRS.

1. Introduction

Aromatic amines are widely used key intermediates in the industrial synthesis of dyes, pharmaceuticals and agrochemicals [1]. A variety of methods for the direct reduction of aromatic nitro compounds to the corresponding amines has been well documented [2–4]. However, development of new methodology especially the environmentally benign process still attracts the great interests in the chemistry community [5–8]. In comparison to the commonly used methods which involve hydrogenation, electron transfer and hydride reduction, photocatalytic reduction emerges as cost-effective, highly selective, rapid and environmentally friendly. Li and co-workers first reported a photoinduced reduction of nitro compounds to the corresponding amines using TiO_2 semiconductor as a catalyst [9]. Ferry and co-workers further investigated the mechanism of photocatalytic reduction of nitro aromatics at the surface of titanium dioxide slurries in the presence of the sacrificial electron donor methanol or isopropanol [10].

Heterogeneous photocatalysis has been rapidly becoming an exciting and growing area of research due to its direct application for synthetic chemistry, such as Photo–Kolbe oxidation [11], reduction [12], amino acid [13], Diels–Alder [14] and Friedel–Crafts alkylation [15] reactions. However, so far these reactions are still hardly applied to the industrial field. Research in our laboratory has focused in the late few years on new active-TiO_2 based reducing systems. The reaction for synthesis of amines from nitro compounds was catalyzed by irradiating N-doped TiO_2 (N-TiO_2) and potassium iodide in solution of methanol (Scheme 1). The procedure of synthesis of aromatic amines was much simpler and more efficient than those in any other literature. In addition, the photocatalyst could be reused and remained sufficient catalytic activity.

2. Experimental

2.1. Catalyst preparation and characterization

All reagents were analytical reagent grade and were used without any further purification. A solution of tetrabutyltitanate (8.5 mL) in absolute ethanol (30 mL) was mixed with glacial acetic acid (1.5 mL) as constraining reagent to prevent the precipitation of oxides and stabilize the solution and an ethanol solution of distilled water and urea ($EtOH:H_2O:CH_4ON_2 = 3:48:1$) was added to above solution under vigorous stirring. The pH of solution was adjusted about three by nitric acid. After 3 h, the gel so obtained had been left ageing overnight at room temperature to ensure the completion of the hydrolysis, subsequently evaporation of the solvent, drying at 100 °C for 8 h and finally calcination at 450 °C for 4 h. The anatase crystal phase was determined from the X-ray diffraction (XRD) patterns obtained by using an X-ray diffractometer (Model D/Max 2550 V) with a Cu target Ka-ray ($\lambda = 1.544178$ Å). The morphology of the N-TiO_2 powders was examined by using a Hitachi-600-2 transmission electron microscope (TEM) and UV–Vis diffuse reflectance spectrophotometer (Cary 300, Varian, US) was employed to determine the optical properties of N-TiO_2 and pure

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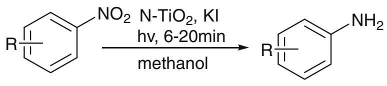
1566-7367/$ - see front matter © 2009 Published by Elsevier B.V.
doi:10.1016/j.catcom.2008.12.045



Scheme 1. Chemical synthesis of aromatic amines with N-doped TiO_2 and KI.

TiO_2. The surface composition and bonding configuration were measured by XPS in a VG ESCALAB250 system.

2.2. Photocatalytic synthesis of aromatic amines

Photocatalytic reactions were carried out in a cylindrical round bottomed quartz photo-reactor and irradiated using 500 W high-pressure mercury lamp and solar light under magnetic stirring at room temperature. The reduction of aromatic nitro compounds (1 mmol) was carried out in the present of N-TiO_2 (10 g/L) and potassium iodide (0.3 mmol) in methanol (30 mL), which was irradiated for 6–20 min. Then while stirring, the reaction mixture became heterogeneous as the reaction progressed. The light yellow N-TiO_2 was filtered and the filtrate was concentrated to dryness. The crude product was further purified by silica-gel column chromatography to give the product amines. All products gave HPLC spectra consistent with the spectra of standard.

3. Results and discussion

3.1. TEM observations and optical properties of N-TiO_2 powders

Fig. 1a shows typical TEM images of anatase N-TiO_2 particles. The characterization of catalyst by TEM studies showed that the nanoparticles were well-distributed. The average size of nitrogen doped TiO_2 nanoparticles was between 5.20 and 13.5 nm which were essentially consistent with the XRD result. The size distribution graphic was depicted in Fig. 1b.

The UV–Vis DRS absorption spectra of N-TiO_2 and TiO_2 were shown in Fig. 2. N-TiO_2 sample absorbed more visible light in the range of 400–550 nm comparing with pure TiO_2, and the method was effective to shift the optical absorption of N-TiO_2 particles toward the visible regions. The band gap of sample is determined by the equation $E_g = 1239.8/\lambda$ [16], where E_g (eV) is band gap and λ (nm) is the wavelength of the absorption edge in the spectrum. The band gaps obtained optically were approximately 2.85 and 3.02 eV for N-doped TiO_2 and TiO_2, respectively, revealing that the band gap of TiO_2 was narrowed by N doping. The absorption edge of N-TiO_2 was moved to 550 nm, resulting in extending the activating spectrum from UV to the visible range. The absorption edge was shifted to the lower-energy region in the spectrum of N-TiO_2. The band gap narrowing in our research may be caused by introduction of nitrogen from urea into the lattice of titanium. Thus, the sample of N-TiO_2 showed the excellent visible light absorption, indicating the increase of photocatalytic activity in visible region.

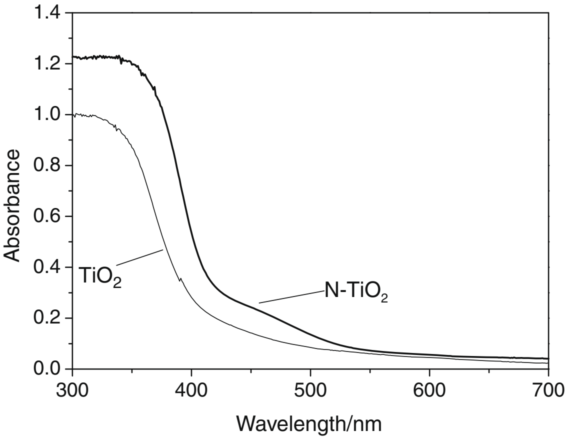


Fig. 2. The UV–Vis diffuses reflectance spectra of N-TiO_2 and TiO_2.

3.2. XRD observations and XPS analysis

Shown in Fig. 3 were X-ray powder diffraction patterns of TiO_2 and N-TiO_2 powder samples prepared. From the intensity ratios between the diffraction appearing at $2\theta = 25.5$ (anatase 101) may conclude that the TiO_2 deposited at 450 °C consists almost completely of the anatase phase and no other crystal phase can be detected. The average crystalline size of N-TiO_2 was calculated using the Scherrer equation. Pure TiO_2 had a particle size of 10.4 nm; doped TiO_2, about 6.80 nm. N-doped TiO_2 powers showed smaller size than undoped-TiO_2 prepared at the same calcination temperature.

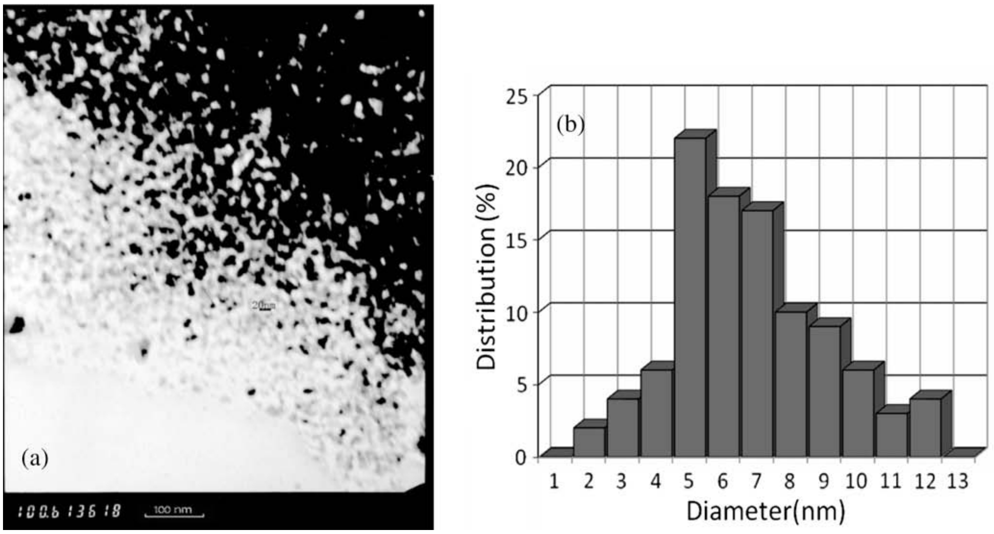


Fig. 1. (a) TEM micrograph of N-TiO_2 nanoparticles. (b) Size distribution of N-TiO_2 nanoparticles determined by TEM. The sizes were determined for 100 nanoparticles selected at random.