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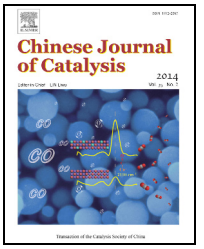

Article

Nanocrystalline titanium dioxide catalyst for the synthesis of azlactones

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ABSTRACT

Titanium dioxide nanoparticles were prepared by a electrochemical reduction method using parameters such as current density, solvent polarity, distance between electrodes, and concentration of stabilizers to control the size of the nanoparticles. The nanoparticles were characterized by UV-Vis spectroscopy, X-ray diffraction, scanning electron microscopy and transmission electron microscopy, and their catalytic performance was tested for the synthesis of a series of 4-aryldiene-2-phenyl-5(4)-oxazolones from the cyclodehydration and condensation of the respective aldehyde, hippuric acid and acetic anhydride. Easy availability, reusability and eco-friendliness were some prominent features of the nanocrystalline titanium dioxide catalyst.

1. Introduction

During the past few decades, many results were published in the area of the synthesis of heterocyclic molecules whose physical and chemical properties make them biologically important [1]. Among these, 2-oxazolin-5-ones (azlactones) are multifunctional compounds that are known to react at the C=C, C=N, C=O bonds, and so they are important for the synthesis of many natural products, synthetic intermediates and pharmaceuticals [2–4]. They are also useful precursors for the synthesis of unsaturated amino acids [5], peptides [6] and biosensors [7]. Substituted oxazole derivatives have been found to be useful for their biological activity such as antibacterial [8], antitubercular [9], anticancer [10] and antitumor [11] activity. Other application of oxazole derivatives includes their use as fluorescent whitening agents, lubricants, dyes and pigments [12–15].

The most common method for their preparation is the Erlenmeyer-Plöchl reaction which proceeds by the cyclodehydration and condensation of the aldehyde and hippuric acid in dry acetic anhydride catalyzed by sodium acetate [16]. The classical reaction has remained unchanged for the last century with only some modernization in the reagents and catalysts, such as the use of supported KF [17], $Bi(OAc)_3$ [18], $Bi(OTF)_3$ [19], [bmim]OH [20], $Ca(OAc)_2$ [21], ZnO NPs[22], alumina [23], KPO_4 [24] or a sonochemical reaction [25]. Each of these advances has its own merits, but they also suffer from drawbacks such as reaction at high temperature, unsatisfactory yields, harsh reaction conditions, and use of stoichiometric amounts of catalyst. Thus the development of a new synthesis strategy which can overcome these drawbacks using an easily accessible catalyst is still important.

Metal nanoparticles are promising materials as the heterogeneous catalyst in a variety of organic transformations [26–30]. Their catalytic properties are functions of their size and crystal lattice parameters and they show amazing levels of performance in terms of selectivity, activity and improved yield of products [31–33]. In particular, titanium dioxide nanoparticles exhibited many special properties because the band gap of the nanoparticles increased with the decrease in size. The

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use of TiO_2 nanoparticles has received considerable attention in green synthetic organic chemistry [34–38] and the photo-degradation of carcinogenic dyes [39] and pesticides [40].

The synthesis of transition metal nanoparticles by the electrochemical reduction method was originally reported by Reetz et al [41], who showed that it gave metal nanoparticles with a narrow size distribution. The cluster size was found to decrease with an increase in current density [42]. The solid product exhibited electronic, paramagnetic, optical and catalytic properties that were significantly better than those of the bulk material, which was due to its extremely small size and large surface area. In the present work, TiO_2 nanoparticles were prepared by the electrochemical reduction method and their catalytic activity was tested for the synthesis of azlactone.

2. Experimental

2.1. Catalyst preparation

All chemicals were purchased from Aldrich and S. D. Fine Chemicals Suppliers and used as received. The purity of the substrates and the reaction monitoring were determined by thin layer chromatography (TLC) and visualization under ultraviolet (UV) light. In the initial experiment we used a titanium metal sheet (1 cm × 1 cm) as anode and a platinum sheet (1 cm × 1 cm) as the cathode. The two electrodes were 1 cm apart. Tetrabutyl ammonium bromide (TBAB, 0.01 mol/L) in an acetonitrile and tetrahydrofuran solution (4:1) was the electrolyte. Upon applying a current density of 10 mA/cm^2, we obtained > 95% of the titanium dioxide clusters getting stabilized by TBAB. Electrolysis was carried out in nitrogen atmosphere. The titanium dioxide nanoparticles were white in color. Since the material was insoluble in the solvent used, the work up only needed simple decantation. The decanted solid product was washed with dry THF three to four times to remove excess tetrabutyl ammonium bromide and dried in a vacuum desiccator. The dried sample was calcined at 550 °C and stored in closed glass vials under ambient conditions.

2.2. Catalyst characterization

The titanium dioxide nanoparticles were characterized by UV-Vis spectrophotometry, XRD, TEM, and SEM-EDS techniques. The wavelength of absorbance was determined by a UV-Vis spectrophotometer [JASCO 503] using a quartz cuvette and an acetonitrile/tetrahydrofuran solution as reference. The IR spectra were recorded on a FT-IR spectrometer [JASCO, FT-IR/4100, Japan] using dry KBr as the standard reference. The XRD patterns of the TiO_2 nanoparticles were recorded on a Bruker 8D advance X-ray diffractometer using Cu K_α radiation of wavelength 0.154 056 nm. To study the morphology of TiO_2 nanoparticles, SEM analysis was carried out with a JEOL (JSM-6330 LA) equipment operated at 20.0 kV and 1.0 nA. The elemental compositions of the TiO_2 nanoparticles were examined using a energy dispersive spectrometer (EDS). The TEM analysis was carried out with a Philips Model CM200 equipment operated at 20–200 kV. ^{1}H NMR spectra were recorded on an 400 MHz FT-NMR spectrometer with $CDCl_3$ as a solvent. The chemical shift values are recorded as δ (ppm units) relative to tetramethylsilane (Me_4Si) as an internal standard.

2.3. Typical reaction procedure

A mixture of an aromatic or heteroaromatic aldehyde (2 mmol), hippuric acid (2 mmol), acetic anhydride (6 mmol) and 100 mg of TiO_2 nanoparticles in 5 ml ethanol was heated with constant stirring at 120 °C. At first the mixture became almost solid and then with increase in temperature, it gradually turned into a deep yellow colored liquid. The progress of reaction was monitored by TLC. After completion of the reaction, 30 ml of hot ethanol was added to the flask to separate out the catalyst. After cooling, the yellow color product was filtered and washed with ice cold ethanol and then with hot water, and dried and recrystallized to afford pure crystals of the desired compound. The products (**3a**–**3m**) were confirmed by comparison with standard samples using the IR, ^{1}H NMR and C^{13}NMR spectra and melting points.

2.4. Spectral data of representative compounds

3a. Bright yellow needles. ^{1}H NMR ($CDCl_3$, ppm) δ = 8.22–8.17 (m, 4H, ArH), 7.55–7.61 (m, 3H, ArH), 7.22–7.39 (m, 3H, Ar-H and –CH=); ^{13}C NMR (101MHz, $CDCl_3$) δ = 110.0, 125.6, 128.4, 128.8, 128.9, 131.2, 131.8, 132.4, 133.3, 133.5, 163.6, 167.6; IR (KBr) ν = 3322, 2930, 1795, 1655, 1165 cm^{-1}.

3c. Yellow needles. ^{1}H NMR ($CDC1_3$, ppm) δ = 7.16 (s, 1H, –CH=), 7.40–7.64 (m, 5H, Ar-H), 7.85 (d, 1H, Ar-H), 8.00 (d, 1H, Ar-H), 8.19 (d, 1H, Ar-H), 8.30 (s, 1H, Ar-H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 125.39, 128.06, 128.58, 129.01, 129.87, 131.12, 31.25, 131.70, 134.02, 134.42, 135.84, 190.25; IR (KBr): ν = 3322, 2930, 1799, 1657, 1165 cm^{-1}.

3f. Bright yellow solid. ^{1}H NMR ($CDCl_3$, ppm) δ = 8.19–8.16 (m, 2H), 8.10 (d, J = 8.1 Hz, 2H), 7.62–7.52 (dd, J = 10.5 Hz, 4.6, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.23 (s, 1H), 2.42 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 21.3, 125.6, 128.6, 128.9, 129.6, 132.1, 132.3, 133.1, 133.3, 133.6, 139.0, 163.5, 167.7; IR (KBr) ν = 3432, 2922, 1791, 1654, 1160 cm^{-1}.

3h. Orange solid. ^{1}H NMR ($CDCl_3$, ppm) δ = 3.87 (s, 3H, CH_3), 7.12 (d, 2H, J = 8.4 Hz, ArH), 7.35 (s, 1H, –CH=), 7.62–7.74 (m, 3H, ArH), 8.12 (d, 2H, J = 8.4 Hz, ArH), 8.32 (d, 2H, J = 8.4 Hz, ArH); IR (KBr) ν = 3432, 2938, 1789, 1654, 1162 cm^{-1}.

3g. Yellow needles. ^{1}H NMR ($CDCl_3$, ppm) δ = 7.39 (d, 1H, J = 7.6 Hz, ArH), 7.48 (s, 1H, –CH=), 7.53–7.66 (m, 4H, ArH), 8.17(d, 2H, J = 7.6 Hz, ArH), 8.90 (d, 1H, J = 8.4 Hz, ArH); IR (KBr) ν = 3448, 3088, 1798, 1658, 1170 cm^{-1}.

3. Results and discussion

3.1. SEM-EDS results

SEM analysis was carried out to study the morphology of the TiO_2 nanoparticles. It can be seen from Fig. 1(a) that the TiO_2 powders have a uniform size and can be classified as nanoparticles. The EDS spectrum was used to analyze the composition