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One-pot synthesis of secondary amine via photoalkylation of nitroarenes with benzyl alcohol over Pd/monolayer $H_{1.07}Ti_{1.73}O_4{\cdot}H_2O$ nanosheets

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ABSTRACT

The photoalkylation of nitroarenes with benzyl alcohols in one pot at room temperature and 1 atm N_2 was achieved over the Pd/$H_{1.07}Ti_{1.73}O_4{\cdot}H_2O$ nanosheets. The sample shows efficient photocatalytic activity with high conversion of nitrobenzene (99%) and selectivity of secondary amine (85%). This flexible photocatalytic system is also applicable to other nitroarenes with high efficiency. Results of in situ FTIR, DRS, and in situ ESR revealed that the benzyl alcohol and nitrobenzene molecules can bind with the surface Lewis and Brønsted acid sites in the catalyst via the $H{-}O{\cdots}Ti$ and $NO_2{\cdots}H{-}O{-}Ti$ species. The formation of surface coordination species results in not only the activation of reactant molecules via surface electron transfer, but also the expanded visible light absorption of the catalyst. Moreover, in situ ESR suggested that the surface coordination can also facilitate the formation of oxygen vacancies in catalysts, which can greatly promote the exposure of Lewis sites and enhance the activation of reactant molecules. Finally, a possible hydrogen transfer strategy over the sample is proposed on a molecular level.

1. Introduction

Tandem catalysis that enables multistep reactions in one pot has attracted great attention because it avoids time-consuming, tedious intermediate separation processes, energy consumption, and waste of production [1,2]. Tandem reactions are widely used in various organic transformations [3], especially the production of secondary amines, because secondary amines and their derivatives are extremely important intermediates for synthesis of pharmaceuticals, agrochemicals, and polymers [2–5]. An attractive route for synthesis of secondary amines is the tandem alkylation of amines in one pot with an alcohol as the alkylating agent [6–8]. Many heterogeneous catalysts have been developed for the alkylation of amines with alcohols, such as Cu—Mo/TiO_2 [9], Pd-ligand [10], Pd/MgO [11], Ir—Zr MOFs [12], Pd/C [13], and Ru$(OH)_x/Al_2O_3$ [14]. However, as typical anilines precursors, the synthesis of secondary amines from nitroarenes still faces great challenges. Very recently, PdAg@MIL-101 [15], Au/TiO_2, Pd/TiO_2, and Pt/TiO_2 [16] have been used as catalysts for the tandem alkylation of amines from nitroarenes. But most of these catalyses were used under hydrogen or at elevated temperature. Therefore, an efficient catalyst is needed for the synthesis of secondary amines from nitroarenes with alcohols in one-pot multistep reactions under mild conditions. This is desirable for green chemistry.

The hydrogenation of nitroarenes to primary amines is the challenging step in such a one- pot multistep reaction under mild conditions. Several reductive methods have been developed to hydrogenate nitroarenes to amines, such as photocatalysis [17] and electrolytic reduction [18]. Photocatalysis has been widely used in the hydrogenation of nitroarenes. In our previous studies, we have developed a series of photocatalysts for the hydrogenation of nitrobenzene and its derivatives to corresponding anilines in water at room temperature and under 1 atm N_2 [19]. In these photocatalytic systems, $(NH_4)_2C_2O_4$ or $HCOONH_4$ was added as a hole scavenger to generate the hydrogen for the reaction. If the photogenerated holes can be consumed by alcohols, producing the corresponding aldehydes, the produced anilines and aldehydes may react to form the secondary amines or imines. How can an appropriate photocatalyst with the strong redox capacities be rationally designed to catalyze coupled alcohol oxidation and nitroarene reduction in such a one-pot multistep reaction?

Recently, Higashimoto and co-workers reported the photosynthesis of imines from benzyl alcohol and nitrobenzene in one pot over TiO_2-based materials [20]. This would provide the possibility of photoalkylation of nitroarenes with benzyl alcohols to produce

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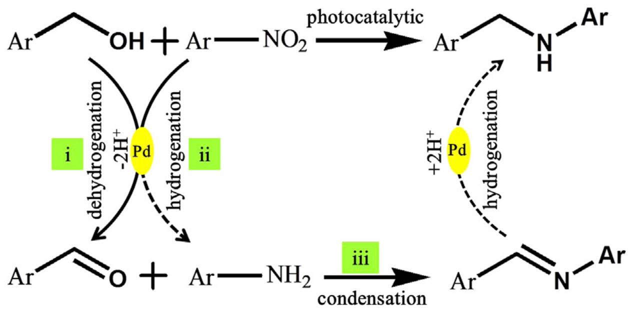
secondary amines. It is reported that the Lewis acid sites in the catalyst can facilitate the reaction between the formed aldehyde and the primary amine to form a secondary amine [20,21]. Furthermore, the Lewis acid sites have been proved to promote the conversion of benzyl alcohol to benzaldehyde [22]. Thus, efficiently exposed Lewis acid sites could be considered in the design of catalysts. Recently, we prepared nanosheets of the lepidocrocite-type monolayer $H_{1.07}Ti_{1.73}O_4{\cdot}H_2O$ (Ti-NS). Ti-NS, with a band gap of 3.4 eV, shows ae strong redox capacity. The valence (VB) and conduction (CB) band of Ti-NS are about −0.88 and 2.42 eV vs. NHE respectively [23]. Moreover, Ti-NS possesses abundant surface Lewis and Brønsted acid sites, resulting in the highly efficient photocatalytic hydrogenation of phenol to cyclohexanone with the assistance of Pd [24]. Therefore, suitable band structure and abundant surface acid sites make Ti-NS a promising candidate for photocatalysis of the synthesis of secondary amines from nitroarenes with alcohols. Based on this, we developed $Pd/H_{1.07}Ti_{1.73}O_4{\cdot}H_2O$ (Pd/Ti-NS) as a photocatalyst for the photo-alkylation of nitroarenes with benzyl alcohol in one pot at room temperature and under 1 atm N_2 (Scheme 1). High conversion of nitroarenes (99%) and selectivity of secondary amines (85%) were achieved over the Pd/NS photocatalyst. Influences on photocatalytic activity have been discussed in detail on in relation to structures, morphologies, superficial properties, and optical properties through XRD, SEM, TEM, XPS, and UV-DRS characterization. The coordination behavior of reagent molecules on superficial Lewis and Brønsted acid sites of catalysts has been revealed by in situ FTIR, in situ ESR, and N_2 adsorption techniques. Furthermore, interfacial electron transfer from reagent molecules to catalysts via surface coordination was also elucidated by UV-DRS, in situ FTIR, and in situ ESR. Finally, a possible photocatalytic mechanism was proposed on a molecular level, which is distinct from that of classic catalysis. This work not only highlights the photocatalytic synthesis of secondary amines from nitroarenes and alcohols, but also may spark the design and construction of efficient photocatalysts for organic synthesis in industry.

2. Experimental

2.1. Reagents and chemicals

Reagents such as TiO_2, metal carbonates, and tetrabutylammonium hydroxide (TBAOH; 40 wt% solution) used in this work were of analytical grade and without further purification. Methanol (CH_3OH, Sinopharm Chemical Reagent Co., >99%), nitrobenzene (Sinopharm Chemical Reagent Co., CP), benzyl alcohol (Aladdin Industrial Inc., AR), 4-chlorobenzyl alcohol (Alfa Aesar, 99%), 4-bromobenzyl alcohol (Aladdin Industrial Inc., 99%), 4-methylbenzyl alcohol (Alfa Aesar, 99%), 4-methoxybenzyl alcohol (Aladdin Industrial Inc., 98%), 4-nitrotoluene (Aladdin Industrial Inc., 99%), 4-nitrophenol (Aladdin Industrial Inc., AR), 3-nitrophenol (Aladdin Industrial Inc., 99%), 2-nitrophenol (Aladdin Industrial Inc., 99%), 4-nitroanisole (Aladdin Industrial Inc., 98%), 1-chloro-4-nitrobenzene (Aladdin Industrial Inc., CP, 98%), 1-bromo-4-nitrobenzene (Aladdin Industrial Inc., GC, >99%), and benzotrifluoride (Aladdin Industrial Inc., 99%) were also used. Deionized (DI) water (~18.2 MΩ cm) was used throughout the experiments.



Scheme 1. Sketch map of photocatalytic N-alkylation from nitrobenzene and benzyl alcohol.

2.2. Preparation of layered $H_{1.07}Ti_{1.73}O_4{\cdot}H_2O$ (Ti-L) and $H_{1.07}Ti_{1.73}O_4{\cdot}H_2O$ nanosheets (Ti-NS)

The preparation of Ti-L and Ti-NS was carried out via a high temperature solid state reaction [23,24]. The Ti-L was synthesized by the proton exchange process from $K_{0.8}Ti_{1.73}Li_{0.27}O_4$. The Ti-NS was obtained through the intercalation and exfoliation process with TBAOH as the intercalation agent. A mole ratio of Ti-L and TBAOH of 1:1.2 was stirred for more than 4 days at ambient temperature. A white Ti-NS colloidal solution was obtained. Next, 1 M HCl solution was added to the colloidal solution for the flocculation of Ti-NS, followed by centrifugal separation and washing with deionized water. After a drying process at 60 °C, the white powder of Ti-NS was successfully prepared.

2.3. Preparation of Pd/Ti-NS

The metal particles loaded on the surfaces of samples were prepared through photodeposition. An aqueous solution of $Pd(NO_3)_2{\cdot}2H_2O$ (10 mg/mL) was injected into a colloidal solution of Ti-NS, and 5 mL methanol was added as a sacrificial agent. After being strongly stirred for 30 min with N_2 as protective atmosphere, the suspensions were irradiated with a Xenon lamp for 4 h. For comparison, the mixed suspensions were irradiated 6 h to obtain a different size of Pd nanoparticles. The products were collected and washed with water several times, and then dried at 60 °C for further characterization and use.

2.4. Materials characterization

X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance X-ray diffractometer with CuKα radiation ($\lambda = 0.15406$ nm). The UV–vis diffuse reflectance spectra (UV–vis DRS) were obtained for the dry-pressed disk samples using a Cary 500 Scan UV–vis spectrophotometer (Varian). The Brunauer–Emmett–Teller (BET) specific surface areas of the samples were measured by nitrogen adsorption/desorption isotherms at 77 K on an Autosorb-1C-TCD physical adsorption instrument (American Quantachrome) using a Micrometrics ASAP 2020 system. Before being analyzed, the samples were degassed under vacuum at 180 °C for 10 h. Transmission electron micrographs (TEM) were obtained using a JEOL JEM-1010 electron microscope operated at an accelerating voltage of 200 kV. Scanning electron micrographs (SEM) were obtained using an FEI Quanta 200F electron microscope. X-ray photoelectron spectroscopy (XPS) analysis was measured on an ESCALAB 250 photoelectron spectroscopy (Thermo Fisher Scientific Inc.) at 3.0×10^{-10} mbar with monochromatic Al*K*α Radiation (E = 1486.2 eV). A tapping-mode atomic force microscope (AFM, Agilent 5500) with Si-tip cantilever was used to evaluate the morphology of the prepared nanosheets on the mica substrate. A 300 W Xe lamp (Beijing Trustech, PLS-SXE300c) was used as a light source.

2.5. Simulated in situ FTIR measurement

The in situ FTIR spectra of nitrobenzene and benzyl alcohol adsorbed onto the samples were determined on a Nicolet Nexus 670 Fourier transform infrared (FT-IR) spectrometer at a resolution