Journal of Catalysis 357 (2018) 247–256

Contents lists available at ScienceDirect

Journal of Catalysis

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

Simultaneous dehydrogenation and hydrogenolysis of aromatic alcohols in one reaction system via visible-light-driven heterogeneous photocatalysis

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ARTICLE INFO

Article history:
Received 29 July 2017
Revised 29 September 2017
Accepted 12 November 2017

Keywords:
Visible light photocatalysis
Semiconductor CdS
Selective oxidation
Selective reduction
Mechanism

ABSTRACT

Photocatalytic selective organic transformation using photoexcited holes and electrons has attracted worldwide interest. Although extensive studies have made significant progress in dehydrogenation of alcohols, hydrogenolysis of alcohols using photoexcited electrons directly constitutes a challenge. Here, photocatalytic selective dehydrogenation and hydrogenolysis of aromatic alcohols into corresponding alkanes/ethers and aldehydes has been achieved by direct use of photoexcited electrons and holes over CdS under visible light irradiation. Compared with other popular visible-light-driven photocatalysts, Sb_2S_3, Bi_2O_3, N-doped TiO_2, $Zn_3In_2S_6$, g-C_3N_4, and Ce_2S_3, the sum of the yields of alkanes and aldehydes over the as-prepared CdS could reach up to 94% after reaction for 4 h. The high photoactivity and stability of CdS toward dehydrogenation and hydrogenolysis of aromatic alcohols can be ascribed to its appropriate band potentials and effective charge separation–transportation. The optimum positions are that the valence band position should be located between oxidation potentials of alcohol/aldehyde and aldehyde/oxidized aldehyde, and the conduction band position should be more slightly negative than reduction potential of alkane/alcohol. During this reaction, the dehydrogenation reaction consumes two holes and produces two protons; the hydrogenolysis process depletes two electrons and two protons. Therefore, a cooperative, cyclical, and efficient reaction system was established.

1. Introduction

As a green and promising technology, photocatalytic reduction and oxidation reactions, based largely on renewable solar energy and mild reaction conditions and environmentally friendly, have recently attracted extensive interest in multiple areas of scientific research, such as physics, materials, chemistry, and biology [1–4]. Recent progress in photocatalytic selective organic transformations demonstrates that this green technique can obtain diverse fine chemicals by selecting appropriate photocatalysts and finer control of reaction conditions than in conventional synthetic pathways [5–8]. Its advantages lie in its ability to avoid environmentally unfriendly heavy metal catalysts, strong chemical oxidants (e.g., Cr^{IV}, ClO^-, and Cl_2), or dangerous reducing gas reagents (e.g., H_2 and CO) and harsh reaction conditions such as high temperature and high pressure [9–11]. It is known that selective oxidation (dehydrogenation) of alcohols is a fundamental but significant reaction for the synthesis of fine chemicals such as aldehydes and their derivatives under O_2 [12–14]. However, a major challenge for achieving industrialization is to restrain the recombination of photogenerated electron (e^-)–hole (h^+) pairs and acquire high selectivity and photocatalytic efficiency [5,6].

Thus, a number of efforts have been made to design composites for inhibiting the recombination of e^-–h^+ pairs and improving charge transport [15–20]. More recently, we have found that photogenerated e^-–h^+ pairs could be separated and utilized efficaciously for simultaneous selective redox aromatic alcohols/nitrobenzene to aldehydes/aniline over a single photocatalyst, CdS [21] or $CdIn_2S_4$ [22], in one reaction system under visible light. It is worth noting that the activity of selective oxidation of alcohols in this cooperative photoredox system is much higher than that in single photocatalytic oxidation under O_2. This proves that the photogenerated e^-–h^+ pairs are separated and utilized effectively in the reaction system. The photoexcited h^+ and e^- offer their own oxidizing and reducing ability and participate in the organic transformation. Consequently, in a photocatalytic reaction system, can aromatic alcohols achieve hydrogenolysis at the same time of

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https://doi.org/10.1016/j.jcat.2017.11.015
0021-9517/

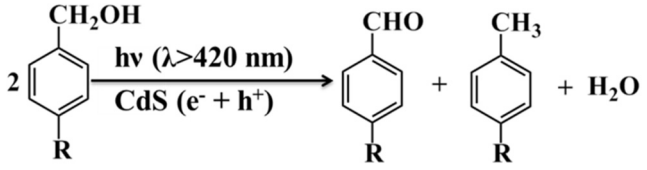
dehydrogenation? How about reduction of aromatic alcohols over photoexcited electrons? Up to now, only one publication [23] has reported photocatalytic dehydrogenation and hydrogenolysis of aromatic alcohols in one reaction system. In that work, semiconductor–metal photocatalysts (Pt/CdS and Pd/$CdS_{0.4}Se_{0.6}$) were used for sunlight-driven dehydrogenation and hydrogenolysis of benzyl alcohol into H_2 and hydrocarbons. However, Pt/CdS favored dehydrogenation over hydrogenolysis to produce H_2, whereas Pd/$CdS_{0.4}Se_{0.6}$ favored hydrogenolysis over dehydrogenation to form toluene. It is hard simultaneously to realize photocatalytic dehydrogenation and hydrogenolysis of alcohols into corresponding alkanes and aldehydes with high selectivity in one photocatalytic reaction system. Moreover, the reaction mechanism has not been clarified up to now.

Here, photocatalytic dehydrogenation and hydrogenolysis of aromatic alcohols (R—Ph—CH_2OH, R=H, Me, OMe, and OEt) into corresponding alkanes/ethers and aldehydes have been achieved in one reaction system by direct use of photoexcited holes and electrons generated on CdS nanoparticles under visible light irradiation under N_2 (Scheme 1). The cooperative photoredox reaction not only represents an efficient, atom-economical, and versatile transformation due to the simultaneous production of easily separable aldehydes and alkanes/ethers under mild conditions, but also can develop a new approach to applying the photoexcited e^-–h^+ pairs and improving the separation efficiency of photogenerated carriers. For instance, the conversion of p-methoxybenzyl alcohol (pMBA) could achieve 100%, and the sum of the yields of p-methoxybenzaldehyde (pMBAD) and p-methylanisole (pMA) could reach up to 94% over the as-prepared CdS photocatalyst under visible light irradiation in only 4 h. The efficient reaction system could also be attained for selective redox of other aromatic alcohols and in different solvents. Moreover, aldehydes and ethers are important fine chemicals that are widely utilized in fragrances and pharmaceuticals and as intermediates in chemical synthesis [6–8,24,25]. Therefore, this photocatalytic reaction toward dehydrogenation and hydrogenolysis of aromatic alcohols is of great value in organic synthesis. Finally, the high photocatalytic performance (activity and stability) of CdS toward dehydrogenation and hydrogenolysis of aromatic alcohols was investigated by a series of control experiments. A possible mechanism was proposed and proved by photoluminescence (PL), reactive-species-scavenger, electron paramagnetic resonance (EPR), and isotopic tracing experiments.

2. Experimental

2.1. Materials

Cadmium nitrate ($Cd(NO_3)_2{\cdot}4H_2O$, 99%), sodium sulfide ($Na_2S{\cdot}9H_2O$, 98.0%), benzotrifluoride ($C_6H_5CF_3$, BTF, 99.0%), p-methoxybenzyl alcohol ($MeOC_6H_5CH_2OH$, pMBA, 98.0%), p-tolylmethanol ($MeC_6H_5CH_2OH$, pTMA, 98%), p-ethoxybenzyl alcohol ($EtOC_6H_5CH_2OH$, pEMA, 98.5%), cyclohexane (C_6H_{12}, 99.5%), methylbenzene ($C_6H_5CH_3$, 98%), acetonitrile (CH_3CN, 99%), phenol (C_6H_5OH, 98.0%), triethanolamine ($C_6H_{15}NO_3$, 98.0%), tetrachloromethane (CCl_4, 99.5%), sodium sulfate anhydrous (Na_2SO_4, 99.0%), and commercial cadmium sulfide (CdS, 98%) were purchased from Aladdin Industrial. 5,5-Dimethyl-1-pyrroline N-oxide (DMPO, ≥97%) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 98%) were purchased from Sigma-Aldrich. Deuterated p-methoxybenzyl alcohol $MeOPhCH_2OD$ (98%) and $MeOPhCD_2OH$ (98%) were purchased from Macklin. All the reagents used in the experiments were of analytical grade and without any further purification. Deionized water used in the synthesis was from local sources.



Scheme 1. Photocatalytic dehydrogenation and hydrogenolysis of aromatic alcohols into corresponding alkanes and aldehydes in one reaction system by direct use of photoexcited holes (h^+) and electrons (e^-) generated on CdS under visible light irradiation.

2.2. Preparation of photocatalysts

Dispersed CdS nanoparticles were prepared by a hydrothermal method. In a typical synthesis, 1.067 g of $Cd(NO_3)_2{\cdot}4H_2O$ was dissolved in 70 mL of deionized water to form a clear solution that was stirred for 30 min at room temperature, followed by the addition of 1.662 g $Na_2S{\cdot}9H_2O$. Afterward, the mixture was stirred for 30 min. transferred to a Teflon-lined stainless steel autoclave with capacity 100 mL, and maintained at 140 °C for 24 h and at room temperature for 24 h, respectively. The obtained precipitates were washed several times with deionized water to remove possible remaining cations and anions before being fully dried at 353 K in an oven. The obtained sample is denoted as CdS-Hy. For comparison, CdS-Pr (CdS-pristine) was also prepared by the same procedure, except for being at ambient temperature (20 °C) instead of 140 °C. The reference samples Sb_2S_3 [26], N-doped TiO_2 (N-TiO_2) [27], $Zn_3In_2S_6$ [28], Ce_2S_3 [29], g-C_3N_4 [30], and Bi_2O_3 [31] were prepared by procedures reported elsewhere.

2.3. Characterization

The phases of CdS samples were analyzed using a Bruker D8 Advance X-ray diffractometer (XRD) using Cu*K*a radiation at 40 kV and 40 mA in the 2θ range from 10° to 80° at a scan rate of 0.05° per second. The optical properties of the sample were characterized by UV–vis diffuse reflectance spectroscopy (DRS) using a UV–vis spectrophotometer (Cary 500, Varian Co.), in which $BaSO_4$ was used as the internal reflectance standard. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were employed to determine the morphology and elemental composition of the sample on an FEI Nova NANOSEM 450 spectrophotometer. Transmission electron microscopy (TEM) images and high-resolution TEM (HRTEM) images were obtained using a FEI Tecnai G^2 F20 S-Twin. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Scientific ESCA Lab250 spectrometer, which consists of a monochromatic Al*K*a (1486.6 eV) beam as the X-ray source, a hemispheric analyzer, and a sample stage with multiaxial adjustability to obtain the surface composition of the sample. All of the binding energies were calibrated by the C1*s* peak at 284.6 eV. Photoluminescence (PL) emission spectra were recorded on a JASCO FP 6500 type fluorescence spectrophotometer with an excitation wavelength of 420 nm at room temperature. Electron paramagnetic resonance (EPR) spectra were measured on a Bruker A300 EPR spectrometer and the same light source as that for the photocatalytic reaction. The Brunauer–Emmett–Teller (BET) specific surface area (S_{BET}) of the sample powders was analyzed by nitrogen adsorption–desorption in a Micromeritics ASAP 2020 apparatus.

2.4. Photoelectrochemical performance

All electrochemical experiments were performed with a CHI 660E electrochemical workstation (CHI Instruments, USA). The photocurrent, electrochemical impedance spectroscopy (EIS), open