Applied Catalysis B: Environmental 238 (2018) 404–409

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Electrostatically mediated selectivity of Pd nanocatalyst via rectifying contact with semiconductor: Replace ligands with light

Tian-Jian Zhao, Wei-Jie Feng, Jun-Jun Zhang, Bing Zhang, Yong-Xing Liu, Yun-Xiao Lin, Hong-Hui Wang, Hui Su, Xin-Hao Li*, Jie-Sheng Chen*

School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China

ARTICLE INFO

Keywords:
Rectifying contact
Photogenerated electric field
Hydrogenation
Furfural

ABSTRACT

Noble metal-based heterogeneous catalysts usually suffered from limited strategies for modifying their selectivity as compared with the homogeneous counterparts. Herein, we reported the electrostatically mediated selectivity of Pd nanocatalyst of usual supported Pd nanoparticles for total hydrogenation of furfural by enhancing the interfacial electric field using visible light and a rectifying contact with semiconductive supports to promote preferred adsorption of C═Ogroups of furfural to the Pd side. This concept-new approach showed the potential to replace traditional organic ligands with light. The Pd nanoparticles deposited on a semiconductor support, optimized to be g-C_3N_4 (Pd/CN) in this work, exhibits outstanding selectivity (≥ 97%) to tetrahydrofurfuryl alcohol, far surpassing the selectivity of reported single-phase Pd nanocatalysts.

1. Introduction

Noble metal-basedcatalysts show high catalytic activity in many reactions with widely applications in the fine chemistry [1–8]. The rational design of myriad amounts of organic ligands to modify the activity and selectivity of metal centers has been well demonstrated in the homogeneous catalytic system, however difficult separation and reusability would result in serious environmental issues [9–12]. Within the regards to real applications in industry and fine chemistry, heterogeneous catalysts are preferred due to their good to excellent reusability and thus relatively lost cost for large-scale uses [13]. Effective strategies for modifying the activity and/or selectivity of heterogeneous Pd nanocatalysts are however still rather limited at the moment. Moreover, the rational control in the selectivity of nanocatalysts for multi-step reactions [14,15], taking the hydrogenation of furfural as a model reaction in this work, has been considered as the key approach to significant depressing the cost of separation or purification for mass production of the target products, but has been less touched till now.

Surface modification strategies have been utilized to tailor the selectivity of noble metal nanoparticles (e.g. Pd nanoparticles) by introducing shape-selective zeolite coatings, specific acid-base nanocomposites of metal oxides or active organic addlayers [16–22]. Precisely control in the crystalline facet and interface of bimetallic structure could also result in unexpected high selectivity of the Pd-based nanocatalysts, even though the complex synthetic methods are not suitable for mass production of these catalysts [23]. Recently, external electric field has been recently applied to trigger the Diels–Alder reaction of conjugated diene and dienophile at the single-molecule level over an Au tip of scanning tunneling microscopy, promising a huge room to further widen the scope of electrostatic-mediated strategy for modifying the activity of metal centers [24]. Herein, we described a photogenerated electric field-mediated approach to tailoring the selectivity of supported Pd nanoparticles with an optimized semiconductive catalyst support for highly efficient hydrogenation of furfural to tetrahydrofurfuryl alcohol in water. This environmentally friendly approach showed the potential to replace traditional organic ligands with light. The rectifying contact between Pd metal and the semiconductor (exemplified with g-C_3N_4 here) could spontaneously initiate the electron redistribution at their interface, which can be further enhanced by the visible light irradiation due to the interfacial Schottky barrier. The enhanced electric field at the Pd-support interface could facilitate the selective adsorption of C = O of furfural on its surface, ensuring the final selectivity to the target product tetrahydrofurfuryl alcohol. Moreover, the ease of mass production, low cost and high chemical stability of g-C_3N_4 benefit the applications of the Pd/g-C_3N_4 nanocomposites as real catalysts for artificial synthesis and even hydrogen production [25–34].

Considering the practical applications of potential heterogeneous nanocatalysts for mass production, a sustainable hydrogenation path of furfural required less energy consumption, zero emission and green

---

* Corresponding authors.
E-mail addresses: xinhaoli@sjtu.edu.cn (X.-H. Li), chemcj@sjtu.edu.cn (J.-S. Chen).

https://doi.org/10.1016/j.apcatb.2018.07.048
Received 17 April 2018; Received in revised form 30 June 2018; Accepted 15 July 2018

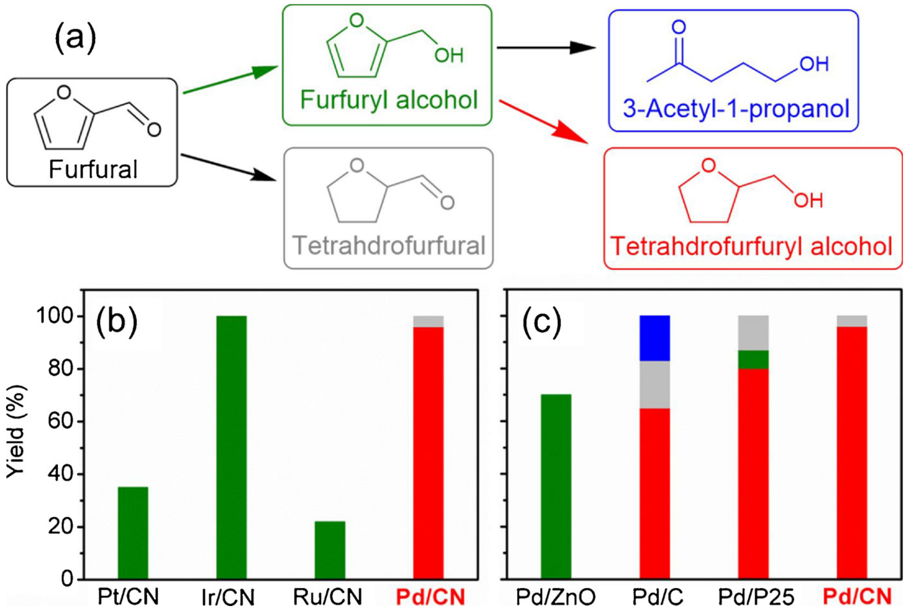

Fig. 1. Screening catalysts for hydrogenation of furfural. (a) Illustration of reaction routes for the hydrogenation of furfural; (b) Screening catalysts with varied metal components (b) and supports (c). Reaction conditions: furfural (0.25 mmol), 8 wt% catalyst (20 mg), H_2O (5 mL), H_2 (1 bar), 8 h, room temperature.

solvents and reactants [35–37]. To this end, we evaluated the catalytic performance of all catalysts for room-temperature and additive-free reactions using water as the solvent and hydrogen gas as the hydrogen source. As presented in Fig. 1a, the hydrogenation of furfural under mild conditions gave at least four products [38–40] among which the furfuryl alcohol was the only product commercial available [29]. As a product of total hydrogenation of furfural, the tetrahydrofurfuryl alcohol was preferred as an organic solvent with less toxic and higher stability or a more processable precursor for the production of bio-fuel [41]. Unfortunately, the selectivity to tetrahydrofurfuryl alcohol over various single-phase noble metal nanocatalysts was still not satisfied as the moment.

2. Experimental section

2.1. Synthesis of mesoporous CN [42–44]

Firstly, 5 g of cyanamide was dissolved in 15 g of Ludox HS40 solution (dispersion of 14 nm SiO_2 particles with 40 wt% in water). The as-formed solution was fast added with ethanol to form white gel. Then the white colloid was placed into crucible and heated at a temperature of 550 °C for 4 h (ramp: 2.3 °C/min) under the protection of N_2 atmosphere. The yellow powders was etched with HF acid (final concentration: 4 M) for one day to remove the silica template. Then the powders were centrifuged, washed three times with distilled water and once with ethanol and finally dried at 60 °C overnight.

2.2. Synthesis of 8 wt% Pd/CN

The as-prepared mesoporous g-C_3N_4 (CN, 100 mg) was dispersed into 40 mL of distilled water with 15 mg of $PdCl_2$ under stir for 12 h. 4 M NaOH solution was added to adjust the pH of the solution to 13. Then, 60 mg $NaBH_4$ was dissolved in 10 mL water and dropped into the as-preparation solution quickly. The solution was stirred for 6 h. Finally, the catalyst was separated by centrifugation and washed with water and ethanol in sequence, and then dried at 60 °C overnight.

2.3. Synthesis of 8 wt% Pt/CN, 8 wt% Ru/CN and 8 wt% Ir/CN

The as-prepared mesoporous g-C_3N_4 (CN, 100 mg) was dispersed into 40 mL of distilled water with 23.94 mg of $H_2PtCl_6{\cdot}6H_2O$, 18.44 mg of $RuCl_3$ or 13.98 mg of $IrCl_3$ under stir for 12 h. 4 M NaOH solution was added to adjust the pH of the solution to 13. Then, 60 mg $NaBH_4$ was dissolved in 10 mL water and dropped into the as-preparation solution quickly. The solution was stirred for 6 h. Finally, the catalyst was separated by centrifugation and washed with water and ethanol in sequence, and then dried at 60 °C overnight.

2.4. Synthesis of 8 wt% Pd/C, 8 wt% Pd/P25 and 8 wt% Pd/ZnO

The catalyst support (100 mg), including carbon (Vulcan XC 72, Cabot), P25 and ZnO, was separately dispersed into 40 mL of distilled water with 15 mg of $PdCl_2$ under stir for 12 h. 4 M NaOH solution was added to adjust the pH of the solution to 13. Then, 60 mg $NaBH_4$ was dissolved in 10 mL water and dropped into the as-preparation solution quickly. The solution was stirred for 6 h. Finally, the catalyst was separated by centrifugation and washed with water and ethanol in sequence, and then dried at 60 °C overnight.

2.5. Preparation of CN and Pd/CN electrode and test

To prepare electrodes, 1.5 mg catalyst and 80 μL of 5 wt% Nafion solutions were dispersed in 1.5 mL of ethanol. The as-prepared mixture was sonicated for 2 h to form a homogeneous ink. Then, 50 μL of catalyst ink was dropped on FTO glasses (1*2 cm2) for twice. After dried up, the FTO glasses were placed in an oven at 120 oC for 1 h. Nafion was not added for the test of Mott-Schottky curves.

2.6. Preparation of CN and Pd/CN electrode and test

The tests of photocurrent responses and Mott-Schottky curves were performed on electrochemistry workstation (CHI660E, China) using a three-electrode electrochemical quartz cell in a 0.5 M Na_2SO_4 solution under simulated sunlight illumination (Perfectlight Tech. Co., Ltd., PLS-SXE300C, 300 W Xe lamp) using long-pass cutoff filters to control the wavelength. The three-electrode electrochemical cell was consisted of Pd/CN or CN, Pt coil and a saturated calomel electrode (SCE), served as working electrode, counter electrode, and reference electrode, respectively. Electrolyte was saturated with N_2 gas before the measurements. And the measured potentials versus SCE were all converted to the