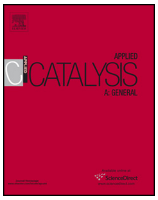
Applied Catalysis A: General 520 (2016) 65–72

Contents lists available at ScienceDirect

Applied Catalysis A: General

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



Preparation and reactivity of UV light-reduced Pd/α-Fe_2O_3 catalyst towards the hydrogenation of *o*-chloronitrobenzene

Weidong Jiang[a,b,*], Bin Xu[a,b], Zhen Xiang[a,b], Xiaoqiang Liu[a,b], Fuan Liu[b]

[a] *School of Chemical and Pharmaceutical Engineering, Sichuan University of Science & Engineering, Zigong 643000, China*
[b] *Key Laboratory of Green Catalysis of Sichuan Institute of High Education, Zigong 643000, China*

ARTICLE INFO

Article history:
Received 5 February 2016
Received in revised form 9 April 2016
Accepted 11 April 2016
Available online 13 April 2016

Keywords:
Catalytic hydrogenation
o-Chloronitrobenzene
UV light-induced reduction
Pd/α-Fe_2O_3 catalyst

ABSTRACT

A type of Pd/α-Fe_2O_3 catalyst was synthesized by a convenient UV light-induced reduction in the presence of Fe^{3+} ions. The synthesized Pd/α-Fe_2O_3 particles were characterized by X-ray diffraction (XRD), low-resolution transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HR-TEM), X-ray photoelectron spectrum (XPS), atomic force microscope (AFM), scan electron microscopy with energy dispersion spectra (SEM-EDS), FT-IR and BET. Related characterizations confirm that UV light-induced reduction is a feasible, simply and environment-friendly method for the preparation of supported catalysts containing active metal. Furthermore, hydrogenation of *o*-chloronitrobenzene (*o*-CNB) to *o*-chloroaniline (*o*-CAN) by the selected Pd(0.5%)/α-Fe_2O_3 was investigated systematically. The α-Fe_2O_3-supported Pd catalyst was found to exhibit good catalytic activity and selectivity for the *o*-CNB reduction under mild conditions. The hydrogenation of *o*-CNB over the resulting Pd-based catalyst gave a 100% *o*-CNB conversion and 91.4% selectivity of *o*-CAN under the reaction conditions of 50 °C, 2 h, 1 MPa hydrogen pressure, $n_{o\text{-CNB}}/n_{Pd} = 6000{:}1$. Moreover, the resulting Pd-based catalyst remained higher hydrogenation reactivity after three runs even if a sharply decrease in activity was observed at the fourth run. The obtained results reveal the as-prepared Pd/α-Fe_2O_3 is an efficient catalyst for the hydrogenation of *o*-CNB even at a high level of substrate concentration.

1. Introduction

The hydrogenation of nitro compounds is commonly conducted to prepare aromatic amines that are important intermediates for dyes, drugs, and agrochemicals [1,2]. Thereupon, many research groups have engaged in the synthetic methods and process of aromatic amines [3]. Especially, the hydrogenation of corresponding nitroaromatics proved to be an easier and convenient route for the production of aromatic amines [4–13]. Hence, many chemists and researchers devoted to the development and improvement of this technology.

For one catalytic reaction two main aspects, including developing efficient catalysts and optimizing reaction conditions, are highly attracted scientist's attention. Noble metal catalysts are well known for their high catalytic activities in hydrogenation reactions [5,7,14–19]. Among these catalysts, palladium-based catalysts were widely used in the reduction of various compounds due to its high activity and selectivity [20–26]. To improve the stability and recyclability of metal catalysts, moreover, almost all active metal components applied in previous works were loaded on the varied supports, such as activated carbon [27], metallic or non-metallic oxidates [15,28–30], polymer [31,32], grapheme [33], etc. At present, chemists focused on the design and preparation of different supports with dazzling morphologies.

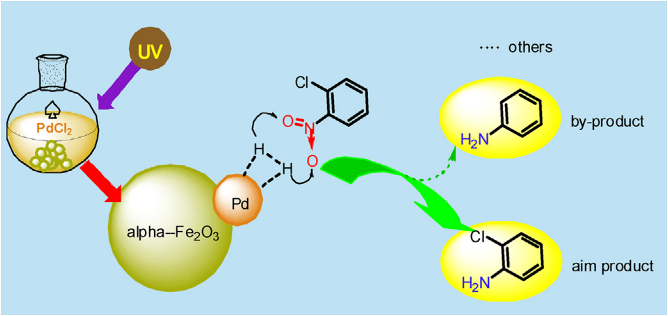
In the catalytic hydrogenation reactions, it was widely accepted that zero-valent metal atoms on the carriers are the real catalysts. This is the reason for a reduction process of cationic metals in the preparation of immobilized metal catalysts. Nowadays, chemical reductants [34,35] were applied in the reduction of metal cations to zero-valent ones. Compressed hydrogen as classic reducing agent is used to reduce metal ions loaded on supports [36], and whereas it is potential flammable and explosive owing to its intrinsic characters. Meanwhile, in the general preparation of supported metal catalysts, chemical reductants are widely applied in the reduction of metal ions. Howbeit, these reductants have their limitations concerning expensive price, environmental hazard and operated dangerous.

Interestingly, Enrico Borgarello et. al reported a facile UV light-induced reduction method [37] for the reduction of metal ions. Nevertheless, this strategy was seldom used in the preparation of

---

* Corresponding author at: School of Chemical and Pharmaceutical Engineering, Sichuan University of Science & Engineering, Zigong 643000, China.
E-mail address: jwdxb@163.com (W. Jiang).

http://dx.doi.org/10.1016/j.apcata.2016.04.007
0926-860X/© 2016 Elsevier B.V. All rights reserved.



Scheme 1. Representation of the *o*-CNB hydrogenation by Pd/α-Fe_2O_3 catalyst prepared by UV light-induced route.

various supported catalysts for the hydrogenation reaction so far. In the present study, we prepared a kind of immobilized Pd catalyst over stable α-Fe_2O_3 using UV light-induced reduction method as a facile and environment-friendly one in comparison with chemical reduction. Furthermore, we evaluated the hydrogenation reactivity of the resulting Pd-base catalyst, systematically. Impact of varied reaction conditions on the hydrogenation was screened for the aim of achieving much higher *o*-CAN yield (Scheme 1).

2. Experimental

2.1. Material and methods

All reagents were of analytical grade and used as received. $PdCl_2{\cdot}2H_2O$ was a product of Kunming Institute of Precious Metals (China). $Fe(NO_3)_3{\cdot}9H_2O$ was purchased from Tianjin Fuchen Chemical Reagents Factory (China). Standard samples of *o*-CNB, *o*-CAN and aniline were purchased from Sigma-Aldrich Co.

2.2. Preparation of α-Fe2O3

The α-Fe_2O_3 carriers were obtained according to following process. $Fe(NO_3)_3{\cdot}9H_2O$ solution (0.1 mol/L) was prepared in deionized water. Ammonia solution was slowly dropped into the $Fe(NO_3)_3{\cdot}9H_2O$ solution using constant-flow pump with stirring, during which the pH value of the mixture was adjusted to 8–9. Afterwards, the mixed solution was heated to remove the residual ammonia. The mixture was cooled down to room temperature, and filtrated under vacuum along with a washing process with anydrous ethanol. The yielded solid was dried under vacuum at 80 °C for 4 h. Furthermore, the dried solid was calcinated in a muffle furnace at 250 °C for 2 h. Ultimately, the desired brown α-Fe_2O_3 powder sample was obtained via grinding operation.

2.3. Preparation of Pd/α-Fe2O3 using facial UV-light reduction route

α-Fe_2O_3 powder was added to the prepared solution of $PdCl_2{\cdot}2H_2O$ (theroretic Pd loading content 0.5%). The mixture was stirred thoroughly under ultraviolet radiation [37] (30W) with a constant wavelength of 365 nm for 24 h. The mixture was filtered and washed with deionized water. The solids obtained were dried in vaccum at 80 °C for 4 h. And then, grinding the dried solids produced the desired α-Fe_2O_3-supported Pd catalyst.

2.4. Structural and morphologic characterizations

Low resolution TEM (JEOL JEM 1200EX working at 100 kV) and high-resolution TEM (FEI Tecnai G2 F20 S-Twin working at 200 kV) were utilized to characterize the morphology of the Pd/α-Fe_2O_3 catalyst. BET areas were recorded on a SSA-4200 Specific Surface Area and Porosity Analyzer (Beijing Builder Electronic Technology Co., Ltd.) with a 30% v/v N_2/H_2 flow using pure N_2 (99.9%) as an internal standard. The crystalline phase of the as-prepared Pd catalyst was recorded on a Bruker D2-PHASER X-ray diffractometer (Germany Bruker AXE) with nickel-filtered Cu Kα radiation (λ = 1.5417 Å, 40 kV, 25 mA) in the 2θ zone of 10–90°, and with a scan speed of 0.06°/sec. Atom Force Microscope (AFM) images were obtained on an E-SWEEP AFM (Hitachi High-Technologies Co., Japan). Scanning Electron Microscope with an EDS detector (Germany Bruker AXE) was measured on a VEGA 3SBU instrument from Tescan Co., Czech Republic. The loading content of Pd metal on the resulting Pd-base catalyst was determined on Spectro Arcos ICP-OES (Germany Spectro Analysis Co., Ltd.).

2.5. Catalytic tests

The catalytic hydrogenation of *o*-CNB was preformed in a 100 ml GYF-60-2 stainless-steel autoclave (China Weihai Autocontrolled Autoclave Ltd.) with a thermocouple and a mechanical stirrer. Reaction reagents and catalyst were added into the stainless-steel reactor before each run. The hydrogenation reaction of *o*-CNB started after the reaction system was heated to the desired temperature.

2.6. Analytical methods for the products

The reaction mixtures were filtrated before the product analysis. The analysis of the obtained organic phase was performed using a SC-3000B-204 gas chromatography (Chongqing Chuanyi Analyzer Co., Ltd., China) equipped with a flame ionization detector (FID) and an SE-54 capillary column (30m × Φ0.53 mm). The oven temperature was tuned to 150 °C, while injector temperature and detector temperature were respectively 260°C and 220 °C. The column temperature was progressively increased from 100°C (3 min) to 220 °C (6 min) with a heating rate of 35 °C/min. Data processing was performed with an HW-2000 chromatography workstation (Nanjing Qianpu Software, China). The major reactant and products were identified by comparison with corresponding authentic samples.

3. Results and discussions

3.1. Varied characterizations of the As-prepared Pd/α-Fe_2O_3 catalyst

To elucidate the structure-activity relation of the synthesized Pd catalyst, it is highly important that the structure characterizations by some classic physical methods, such as XRD, SEM, element mapping, TEM, XPS, AFM, etc. As shown in Fig. 1, it was found that the crystalline phase of Pd/α-Fe_2O_3 catalyst is almost the same as that of the used support, α-Fe_2O_3. The X-ray diffraction peak of nano α-Fe_2O_3 at 2θ = 24.16°, 33.11°, 35.62°, 40.86°, 49.46°, 54.11°, 57.60°,62.34°, 64.02°, 71.89°, and 75.34° are assigned to the scattering from (012), (104), (110), (113), (024), (116), (018), (214), (300), (101), and (220) planes and well match with the JCPDS card no.89-596. No crystal phase of Pd was detected by XRD analysis, which is mainly due to two reasons. The one is that the particle size of the Pd(0) species were too small to be detected as well the metallic Pd(0) exhibited amorphous-like or less ordered structural features. Another one is that high dispersion of metallic Pd (0) on the surface of supports leads to no characteristic peaks of metal species that can be used for the observation in the XRD spectra. Therefore, average crystallite sizes of metallic Pd species cannot be estimated on the basis of the XRD patterns using the Scherrer equation.