

Role of bonding mechanisms during transfer hydrogenation reaction on heterogeneous catalysts of platinum nanoparticles supported on zinc oxide nanorods



Reem A. Al-Alawi^{a,b}, Karthik Laxman^{a,c}, Sarim Dastgir^{b,d}, Joydeep Dutta^{a,e,*}

^a Chair in Nanotechnology, Water Research Center, Sultan Qaboos University, PO Box 17, Al-Khoudh, Muscat 123, Oman

^b Department of Chemistry, College of Science, Sultan Qaboos University, PO Box 36, Al-Khoudh, Muscat 123, Oman

^c Department of Electrical and Computer Engineering, College of Engineering, Sultan Qaboos University, PO Box 33, Al-Khoudh, Muscat 123, Oman

^d Qatar Environment and Energy Research Institute, PO Box 5825, Doha, Qatar

^e Functional Materials Division, Materials- and Nano Physics Department, ICT School, KTH Royal Institute of Technology, Isafjordsgatan 22, SE-164 40 Kista, Stockholm, Sweden

ARTICLE INFO

Article history:

Received 15 February 2016

Received in revised form 15 March 2016

Accepted 19 March 2016

Available online 22 March 2016

Keywords:

Heterogeneous catalyst
Hydride transfer reaction
Surface energy
Interface
Supported catalyst

ABSTRACT

For supported heterogeneous catalysis, the interface between a metal nanoparticle and the support plays an important role. In this work the dependency of the catalytic efficiency on the bonding chemistry of platinum nanoparticles supported on zinc oxide (ZnO) nanorods is studied. Platinum nanoparticles were deposited on ZnO nanorods (ZnO NR) using thermal and photochemical processes and the effects on the size, distribution, density and chemical state of the metal nanoparticles upon the catalytic activities are presented. The obtained results indicate that the bonding at Pt-ZnO interface depends on the deposition scheme which can be utilized to modulate the surface chemistry and thus the activity of the supported catalysts. Additionally, uniform distribution of metal on the catalyst support was observed to be more important than the loading density. It is also found that oxidized platinum Pt(IV) (platinum hydroxide) provided a more suitable surface for enhancing the transfer hydrogenation reaction of cyclohexanone with isopropanol compared to zero valent platinum. Photochemically synthesized ZnO supported nanocatalysts were efficient and potentially viable for upscaling to industrial applications.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

A catalyst increases the rate of a reaction by providing alternative routes which collectively lower the activation energy of the primary reaction [1]. Each step is governed by the chemical potential and state of the catalyst surface that are tuned to selectively trigger reactions [2–4]. This is particularly true for supported catalysts which are commercially important and have been widely used in the industry as they facilitate easy recovery [5]. While supported catalysts come in different forms, a popular choice comprises of transition metal/oxide nanoparticles (MNPs) deposited on semiconductor oxide supports [6–9], wherein the surface of the MNP forms the active site for the catalytic reaction [10]. The role of the oxide support is primarily to improve the MNP distribution

and loading, but previous studies have shown that it can also partially contribute towards the catalyst efficiency and selectivity [2]. Further, MNPs deposited on nanorod shaped supports have been observed to exhibit higher surface energy and increased catalytic efficiency [11], suggesting that nanorod morphology is favorable as a support. Nanorods are typically monocrystalline [12] or polycrystalline [13] in nature, wherein their ordered structure promotes charge transfer and easy access to their surface during a catalytic reaction [10].

While several materials can be synthesized as nanorods [14–16], zinc oxide (ZnO) remains the most popular due to its versatility and facile synthesis process [17–33]. The effective surface energy of a ZnO nanorod (ZnO NR) supported catalyst depends on the distribution and interfacial chemistry between the nanorod and the MNP, making it sensitive to the metal deposition [34,35] and post treatment processes [34,36]. Further, the structure of the MNPs itself has a significant effect on the catalyst activity, where recent reports have indicated that metal-hydroxides [37] and layered double hydroxides [38,39] provide a high energy surface for catalytic activities. In fact several processes ranging from co-precipitation

* Corresponding author at: Functional Materials Division, Materials- and Nano Physics Department, ICT School, KTH Royal Institute of Technology, Isafjordsgatan 22, SE-16440 Kista, Stockholm, Sweden.

E-mail address: joydeep@kth.se (J. Dutta).

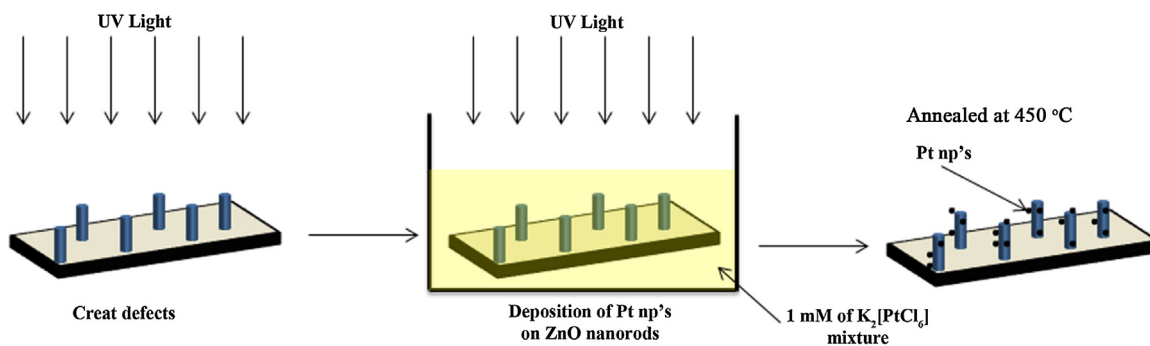


Fig. 1. Deposition of Pt nanoparticles on ZnO nanorods by creating defects on ZnO NRs after exposed to UV-C-light irradiation and then dipped in $K_2[PtCl_6]$ mixture and exposed to UV-C-light irradiation.

[37,40] to laser ablation [39] and exfoliation [38] are detailed in literature to preferentially synthesize metal-hydroxide catalysts which have well distributed active sites and a high surface energy.

In this work, we focus on the preparation of ZnO NR supported platinum catalysts, wherein the surface activity and hydroxide content of the mixed-catalyst is modulated using thermal and photo-mediated surface modification schemes. The effect of the deposition method is studied by using a model reaction involving the transfer hydrogenation reaction of cyclohexanone with isopropanol which proceeds with the reduction of multiple bonds of an organic molecule acting as a hydrogen donor [41–46]. The surface chemical properties of the catalysts are correlated to the catalyst performance for the model chemical reaction studied in this work.

2. Experimental

2.1. Materials

All the chemicals used for synthesis of the catalysts were of analytical grade and used as-received without further purification. Chemicals used in this work include: Zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) and hexamethylenetetramine ($(CH_2)_6N_4$) obtained from Merck, Germany. Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) from Acros Organics and potassium hexachloroplatinate ($K_2[PtCl_6]$) from BDH Chemicals, UK.

2.2. Growth of zinc oxide nanorods (ZnO NRs)

Growth of ZnO NRs on glass slides (used as substrates) was carried out by seeding the substrates with ZnO nanoparticles, followed by extended liquid epitaxial growth in zinc nitrate and hexamine solution. Seeding was carried out using spray pyrolysis with zinc acetate solution (10 mM in water) at a flow rate of 0.25 mL h^{-1} at 350°C . The seeded slides were subsequently cooled to room

temperature and then stored in an oven at 90°C until further use. During the growth of nanorods, seeded glass substrates were placed horizontally in a beaker filled with equimolar (10 mM) solution of zinc nitrate and hexamine. The beaker was placed in a shaker at 90°C at 40 rpm for 5 h. Following the growth of nanorods, the substrates were rinsed several times with distilled water and then annealed at 350°C for 1 h in the ambient prior to further use.

2.3. Preparation of platinum(IV) stock solution

Potassium hexachloroplatinate ($K_2[PtCl_6]$) (19.44 mg, $40 \mu\text{mol}$) was dissolved in 10 mL de-ionized water with sonication for 20 min. 6.25 mL of the solution was added to 18.75 mL EtOH to obtain 1 mM Pt(IV) complex growth solution. The mixture was aged for 70–90 h under white light illumination (1.2 klux).

2.4. UV-C photochemical reduction of Pt on defective ZnO NRs (Catalyst A)

UV-C mediated defect engineering was carried out for 30 min during which the ZnO substrate was exposed to UV-C light irradiation ($\sim 250 \text{ nm}$ wavelength, 12 W) from a distance of 3 cm. Subsequently, the ZnO substrates were dipped in 1 mM Pt complex and placed under UV-C-light for 15 min (Fig. 1). After deposition of the Pt precursor the sample was annealed at 450°C for 1 h in ambient air.

2.5. Solvothermal reduction of Pt on ZnO nanorods (Catalyst B)

Solvothermal deposition of platinum nanoparticles on ZnO NRs were carried out for 15 min during which the ZnO NRs were dipped into 1 mM Pt(IV) complex and simultaneously placed in a water bath heated to 60°C (Fig. 2). Self-assembled Pt nanoparticles on

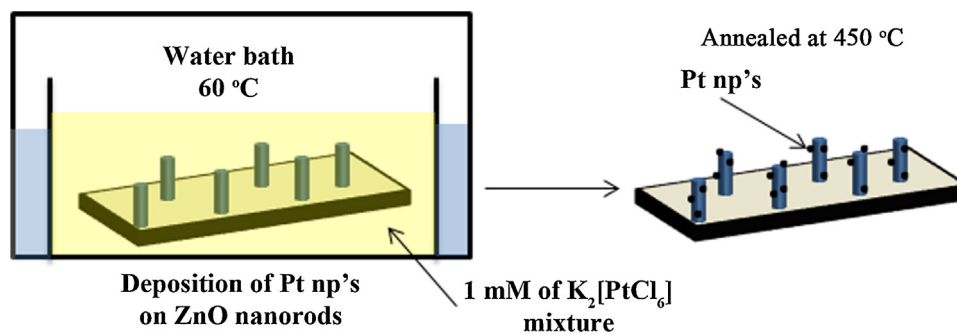


Fig. 2. Deposition of Pt nanoparticles on ZnO nanorods by dipping ZnO NRs substrate in $K_2[PtCl_6]$ mixture and placed in a water bath heated to 60°C .

Download English Version:

<https://daneshyari.com/en/article/5348768>

Download Persian Version:

<https://daneshyari.com/article/5348768>

[Daneshyari.com](https://daneshyari.com)