Journal of Catalysis 364 (2018) 69–79

Contents lists available at ScienceDirect

Journal of Catalysis

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

Palladium nanoparticles supported on core-shell and yolk-shell Fe_3O_4@nitrogen doped carbon cubes as a highly efficient, magnetically separable catalyst for the reduction of nitroarenes and the oxidation of alcohols

Siyavash Kazemi Movahed, Noushin Farajinia Lehi, Minoo Dabiri *

Faculty of Chemistry and Petroleum Sciences, Shahid Beheshti University, Tehran 1983969411, Islamic Republic of Iran

ARTICLE INFO

Article history:
Received 21 January 2018
Revised 30 April 2018
Accepted 2 May 2018

Keywords:
Carbon
Reduction
Oxidation
Magnetic separation
Nanocubes
Heterogeneous catalysis

ABSTRACT

The preparation of palladium nanoparticles (Pd NPs) supported on Fe_3O_4@nitrogen doped carbon (*N*-C) core-shell (C-S) and yolk–shell (Y-S) nanostructures is reported. The Fe_3O_4@*N*-C@Pd C-S nanostructures were synthesized by two different methods. The first method included two steps: (*i*) the annealing treatment of the Fe_2O_3@polydopamine (PDA) under a gas mixture of Ar/H_2 flow and (*ii*) the decorating Pd NPs on the surface of annealed structures by sodium borohydride as a reducing reagent. The second method, the *in-situ* reduction of Fe_2O_3 and Pd^{2+} in the structure of Fe_2O_3@PDA@Pd^{2+} by annealing treatment under H_2 flow as a reducing reagent led to Fe_3O_4@*N*-C@Pd C-S nanostructure. Additionally, the Y-S nanostructures were synthesized by using a HCl solution as an effective etching reagent to the partially etch the Fe_3O_4. Four types of Pd-based catalysts were tested in the selective reduction of *p*-nitrophenol (*p*-NP) to *p*-aminophenol (*p*-AP). Different catalytic activities were obtained through these catalysts. Furthermore, the reduction of nitroarenes and the oxidation of benzylic alcohols were also studies.

1. Introduction

Tailoring the morphology of inorganic nanocrystal's have long been an attractive field of nanoscience and technology [1]. In particular, magnetic NPs with unique size- and shape-dependent magnetic properties inspired an intensive exploration of their potential applications in the past decade [2,3]. Numerous composites have been extensively investigated for their magnetic nanostructures including pure metals (Fe, Co, and Ni), metal oxides (Fe_3O_4 and γ-Fe_2O_3), MFe_2O_4 (M = Cu, Ni, Mn, and Mg), and metal alloys (FePt and CoPt) [4,5]. Among these magnetic NPs, ferrite (Fe_3O_4) nanoparticles have been widely used experimentally for numerous applications such as in the separation of biomolecules [6], drug and gene targeting [7], tissue engineering [8], magnetic resonance imaging [9], magnetic biosensors [10], biocatalysts [11], wastewater treatment [12], supports in heterogeneous catalysts [13], and as mediators of heat for cancer therapy [14]. The naked NPs tend to aggregate to form larger particles because of Van der Waals forces, resulting in a significant deterioration of their original activity [15]. When metal (0) NPs are supported on the bare surface of ferrite, the involvement of iron in the redox processes causes a significant decrease in catalytic activity [16]. Therefore, the Fe_3O_4 have been preferentially coated with catalytically inert materials such as polymer, carbon or silica to support the transition metal nanoparticles [17].

Dopamine (DA) is a biomolecule that contains catechol and amine functional groups, can self-polymerize at alkaline pH values under the oxygen atmosphere. The conformal and continuous polydopamine (PDA) shell can be spontaneously fixed onto various substrates and nanostructures such as hematite, ferrite, etc. due to the high binding affinity of catechol derivative anchor groups (phenolic hydroxyl) to iron oxide just through immersing the particles into the dopamine solution at room temperature [18]. It is also an excellent carbon source that can yield thin *N*-doped carbon coatings with similar structures and electrical conductivities compared to that of *N*-doped multilayered graphene. Metal salts could be readily adsorbed onto PDA surfaces or absorbed into PDA nanostructures, leading to metal-containing *N*-doped carbon nanostructures by carbonization [19].

Palladium catalysts have been developed, and widespread applications in organic transformations, including oxidation [20], alkylation [21], hydrogenation [22], hydroformylation [23], carbonylation [24], and cross-coupling reactions [25]. As a result of

* Corresponding author.
E-mail address: m-dabiri@sbu.ac.ir (M. Dabiri).

https://doi.org/10.1016/j.jcat.2018.05.003
0021-9517/

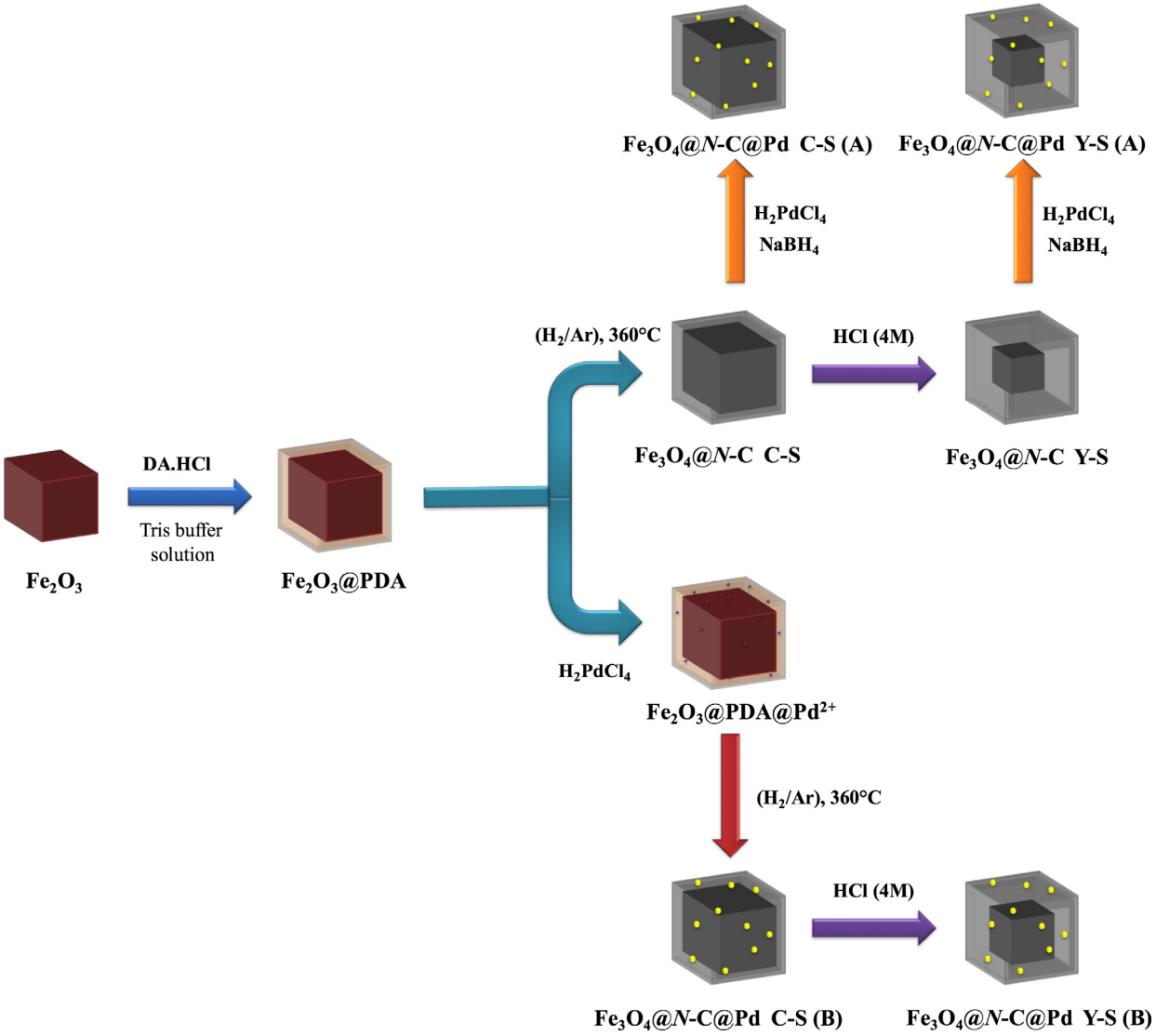
the toxicity and high price of Pd, in recent years, interest has grown in the organization and use of recoverable heterogeneous Pd catalysts. For this purpose, different solid materials such as modified silicas [26], zeolites [27] molecular sieves [28], polymers [29], mesoporous materials [30], ionic liquids [31], activated carbon [32], and natural supports [33] have been used as supports for the heterogenization of Pd catalysts.

Core-shell (C-S) and yolk–shell (Y-S) structured materials with tailored physical and chemical properties have shown great potential for a variety of applications including catalysis, drug delivery, energy storage and conversion [34–39]. Based on this introduction and also as part of our ongoing studies on the synthesis of carbon-based nanocomposite catalysts [40], herein, we report the successful synthesis of unique Fe_3O_4@*N*-C@Pd C-S and Y-S cubes. The proposed synthetic strategy for the preparation of Fe_3O_4@*N*-C@Pd C-S and Y-S is illustrated in scheme 1. The uniform Fe_2O_3 cubes were coated with PDA to obtained Fe_2O_3@PDA C-S cubes followed by transforming into Fe_3O_4@*N*-C C-S cubes after an annealing treatment under a gas mixture of Ar/H_2 flow. The Fe_3O_4@*N*-C Y-S was synthesized by the partial etching of the Fe_3O_4 core in Fe_3O_4@*N*-C C-S structure by using HCl. The Fe_3O_4@*N*-C@Pd C-S and Fe_3O_4@*N*-C@Pd Y-S structures were prepared using two different methods. In the first method, the Fe_3O_4@*N*-C@Pd C-S (A) and Fe_3O_4@*N*-C@Pd Y-S (A) structures were obtained from reducing H_2PdCl_4 with $NaBH_4$ over Fe_3O_4@*N*-C C-S and Fe_3O_4@*N*-C Y-S structures, respectively. For the second method, the Fe_3O_4@*N*-C@Pd C-S (B) was obtained from the *in-situ* reduction of the Fe_2O_3 and Pd^{2+} in the structure of Fe_2O_3@PDA@Pd^{2+} by using H_2 as a reducing reagent. Furthermore, the Fe_3O_4@*N*-C@Pd Y-S (B) was synthesized *via* the partial etching of the Fe_3O_4 core of Fe_3O_4@*N*-C@Pd C-S (B) nanostructure using HCl.

2. Experimental

2.1. Instrumentation

Diffraction data were collected on a STOE STADI P with scintillation detector, secondary monochromator and Cu-Ka1 radiation (λ = 1.5406 Å). Field emission scanning electron microscopy (FESEM) images were characterized using an electron microscope ZEISS SIGMA VP-500. Transmission electron microscopy (TEM) images were characterized using a transmission microscope Philips CM-30 electron microscope with an accelerating voltage of 150 kV.



Scheme 1. Schematic illustration of the formation procedure of Fe_3O_4@*N*-C@Pd C-S (A), Fe_3O_4@*N*-C@Pd Y-S (A), Fe_3O_4@*N*-C@Pd C-S (B), and Fe_3O_4@*N*-C@Pd Y-S (B) nanostructures.