One step synthesis of Pd/Pt nanoparticles for hydrogenation processes

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An eco-friendly method has been developed for the synthesis of bimetallic palladium/platinum nanoparticles. The nanoparticles were synthesized using a bioconjugate, chitosan-poly(3-hydroxybutyrate). The conjugate has both reducing and stabilizing properties owing to the presence of different funtional groups in it, which also assists in enhancing the catalytic activity of bimetallic naoparticles. The synthesized nanoparticle shows improved catalytic activity for hydrogenation process.

Keywords: Green synthesis, bimetallic nanoparticles, biopolymers, hydrogenation, catalysts

Introduction

In the last few decades the green synthesis of nanomaterials has gained attention of researchers to eliminate or at least minimize the use of materials that are potentially toxic to humans and for the environment. Bimetallic nanoparticles when compared with monometallic nanoparticles show unique physical and chemical properties, which can play a key role in heterogeneous catalysis, especially in the hydrogenation field. Chitosan is one of the most abundant polymers in nature and it is mainly produced from crustaceans shell waste. Poly(3-hydroxybutyrate) (PHB) is a member of polyhydroxyalkanoates, it is synthesized by various bacteria and similarly to chitosan can be obtained from waste material [1]. PHB is currently used in drug delivery, as a stabilizing agent, bioplastic and as carbon source and electron donor in *in situ* bioremediation [2]. Due to the superior catalytic behavior of platinum and palladium both were chosen to create bimetallic nanoparticles by green synthesis. Chitosan-polyhydroxybutyrate (Chit-PHB) was chosen due to its remarkable properties that were showed in the catalytic hydrogenation of 4-nitrophenol in our previous work [3].

1. Materials and methods

1.1 Reagent and solution

Chitosan (Physical form 75-85% deacetylated, low molecular weight 50 – 190 kDa), Platinum(II) chloride and (≥99.9%), Potassium tetrachloropalladate(II) (98%), 4–nitrophenol (ReagentPlus >99%) and sodium borohydride (98%) were purchased from Sigma-Aldrich, Polyhydroxybutyrate (PHB, Biomer® P209) was purchased from Biomer (Krailing, Germany). Nitric acid (65%) was purchased from Lachner. Deionised water

1.2 Analytical

SEM (UHR FE-SEM Carl Zeiss ULTRA Plus, Germany) operating at an acceleration voltage 0.5–2.5 kV was used to study the composition and morphology of the Pd/Pt nanoparticles, energy–dispersive X–ray spectroscopy (EDX) analysis was conducted using an EDX system (Oxford Instruments, AZtec) with X–Max detector attached to a Scanning Electron Microscope.

UV-Vis spectrophotometers (Hach Lange DR 3900) with matched 1 cm quartz cells (cuvettes) were used for recording the absorption spectra.

1.3 Conjugate preparation

The conjugate have been prepared following the procedure reported previously by our group [3].

1.4 Nanoparticles synthesis

The synthesis was carried out by adding a certain amount of Chit-PHB (10 g/l) in a close vial containing both palladium and platinum precursors. The vial was heated at 130 °C for 30 minutes, the color of solution shifts from pale yellow to dark brown due to the bimetallic nanoparticles formation.

1.5 Hydrogenation test

The catalytic test for the hydrogenation of 4-nitrophenol to 4-aminophenol by $NaBH_4$ was carried

out in a standard quartz cuvette (1 cm path length). Test was carried out by adding 24 µL of 4-nitrophenol (5 mM) in Eppendorf tube (1.5 ml) and mixed with 6 µL of nanoparticles. Then in an Eppendorf tube 120 µl of $NaBH_4$ (0.1 M) was added and the volume was adjusted to 1 ml by adding DI and mixed. Then the solution was immediately transferred in a quartz cuvette and the Abs was recorded by UV-Vis (Hach Lange DR 3900) at regular intervals. All tests were carried out at room temperature (25 °C).

2. Results and discussion

2.1 SEM

The morphology and the composition the nanoparticles were analyzed by SEM and EDX analysis. Nanoparticles show a spherical shape, while EDX show us presence of both metals palladium and platinum.

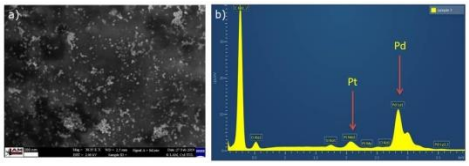

Figure 1 SEM and EDX analysis of bimetallic Pd/Pt nanoparticles (the synthesis was carried out using ratio 1 : 1 (Pd : Pt), 130 °C, 10 g/l Chit-PHB).

2.2 Catalytic activity

To test the catalytic activity of bimetallic nanoparticles hydrogenation test of 4-nitrophenol to 4-aminophenol was carried out. In order to determine the catalytic kinetics of nanoparticles the pseudo-first-order kinetics was applied. The rate constant was calculated from the linear plot of ln(At/A0) versus time (min), the k_{app} was estimated to be 1.83 min^{-1} for the bimetallic nanoparticles synthesized with ratio 1 : 1 (Pd : Pt) at 130 °C.

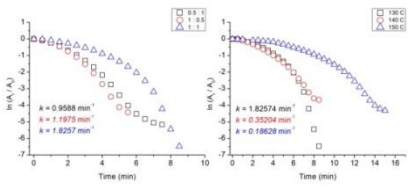

Figure 2 Catalytic hydrogenation of 4-nitrophenol in the system containing Pd/Pt synthesized by different ratio of precursors and different temperatures.

In order to get information about the catalytic activities of these nanoparticles a comparison of different precursors ratio (0.5 : 1, 1 : 0.5 and 1 : 1) and different temperatures (130, 140 and 150 °C) were carried out. From the Figure 2 rate constants of nanoparticles synthesized in ratio 1 : 1 (Pd : Pt) at 130 °C has better results.

3. Conclusions

The present work focuses on using a green approach to synthesize bimetallic Pd/Pt and their use for hydrogenation processes. Bimetallic nanoparticles were synthesized from K_2PdCl_4 and $PtCl_2$, the conjugate not only reduce both salts but also plays a key role in the stabilization of nanoparticles. The optimal synthesis conditions were found to be ratio 1 : 1 of salts precursor, 130 °C and Chit-PHB concentration of 10 g/l. These nanoparticles thus obtained were used for catalytic hydrogenation of nitrophenol.

Acknowledgment

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Reference

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