



Short communication

“Cat in a bag” recycling of dendrimer encapsulated Au nanoparticles by use of dialysis membrane bag in the reduction of 4-nitrophenol: proof of heterogeneous catalysis



Mulisa Nemanashi, Reinout Meijboom*

Department of Chemistry, University of Johannesburg, P.O. Box 524, Auckland Park, 2006 Johannesburg, South Africa

ARTICLE INFO

Article history:

Received 23 February 2016

Received in revised form 18 April 2016

Accepted 12 May 2016

Available online 13 May 2016

Keywords:

Dendrimer

Gold

Heterogeneous catalysis

Nitrophenol reduction

ABSTRACT

Generation 4 PAMAM-NH₂ dendrimers were used as template to synthesize Au₁₃- and Au₁₀₀-dendrimer-encapsulated nanoparticles (Au-DENs) with an average diameter of 2.1 ± 0.3 and 3.1 ± 0.5 nm respectively. Au-DENs were characterized using various techniques. Catalytic recycling of Au-DENs using a dialysis membrane bag in the reduction of 4-NP is presented. The reduction process was primarily monitored by UV–vis spectroscopy at around λ 400 nm. The catalyst was found to exhibit a very good activity and stability even after more than 3 catalytic reaction cycles without any leaching, confirming that the reduction of 4-NP is purely a heterogeneous reaction.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Over the years, transition-metal-based homogeneous catalysts have proved to produce well-defined, highly active and selective catalysts [1]. However, the separation of these homogeneous catalysts from the reaction products can be very costly or difficult and as a result, their commercial application is limited. In the past decades, metal nanoparticles (NPs) consisting of noble metals such as Pt, Ir, and Au, have drawn a lot of attention from researchers due to their unique properties and applications that cannot be achieved by their bulk counterparts [2]. The use of these NPs as catalysts for a variety of organic and inorganic reactions has been extensively investigated [3–5]. NPs can be synthesized using different methods such as co-precipitation [6], micro-emulsion [7] and template [8] methods. Dendrimers have been reported to provide a convenient platform for the synthesis of well-defined NPs with both high stability and a narrow size distribution without passivation of the active metal sites [8,9]. This is attributed to the fact that dendrimers have a well-defined three dimensional structure and their surface functionality can be varied [10]. Although these dendrimers are commercially available, their use with precious metals such as Au, Pt and Pd in catalysis can be very costly. It would be interesting to find a method in which these nano-composite catalysts can be recovered and re-used in solution catalysis.

Researchers have used the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AMP) as a model reaction to study the catalytic

behaviour of NPs [11–14]. This reaction allows a precise kinetic evaluation of NPs since it proceeds in a well-defined manner from a single substrate to a single product. Because nitrophenols are prevalent organic hazardous pollutants in waste-waters generated from agricultural and industrial sources [15] their removal from water using environmental friendly methods is still of great significance in the scientific field. More importantly, the reduction product, 4-AMP, is a useful intermediate in both industrial and pharmaceutical companies [16,17]. Some authors have modelled this reduction reaction in terms of the Langmuir–Hinshelwood (L.-H.) mechanism. For instance, Ballauff and co-workers have reported a number of studies on the catalytic evaluation of NPs in the reduction of 4-NP was modelled in terms of the afore-mentioned mechanism [18–20]. In the L.-H. mechanism, both reactants (borohydride and 4-NP in this case) must first be adsorbed on the surface of the catalysts before the reaction can proceed. Although we, and other authors, have reported on the use of dendrimer-NPs composite as “homogeneous” catalysts for the reduction of 4-NP [21–23], none of these studies has reported a method in which these dendrimer-nanocomposite catalysts can be recovered from the reaction products and be re-used as required by “green chemistry”. However, it is noteworthy to mention that other authors have previously reported the recyclability of dendritic polymer protected thermoresponsive AuNPs in the reduction of 4-NP by NaBH₄ [24]. The AuNPs displayed excellent activity and 95% conversion was achieved even after 6 reaction cycles. The reaction rate for the reduction of 4-NP was found to be accelerated by increasing the reaction temperature. Catalyst recycling was achieved by simply heating the reaction solution at temperature above lower critical solution temperature (LCST) after each catalytic run until the solution becomes turbid.

* Corresponding author.

E-mail address: rmeijboom@uj.ac.za (R. Meijboom).

The thermoresponsive AuNPs were precipitated by centrifugation and be re-dissolved in water for the next catalytic reaction cycle. In another study, the recyclability of polymer protected AuNPs was reported for the biphasic reduction of 4-NP [25]. In this case, the catalyst was recovered from the reaction mixture by its extraction to the organic phase using chloroform (CH_2Cl_2) solvent and reused for the next catalytic reaction. Recently, polymer stabilized AuNPs prepared using a similar method have also been reported to exhibit high activity for the catalytic reduction of 4-NP [26]. However, no recyclability of AuNPs was conducted in that study. Additionally, the question about whether NPs catalysed reaction follows a homogeneous or heterogeneous mechanism remains open for debate [27]. For example, Mahmoud et al. reported that the reduction of 4-NP follows heterogeneous type mechanism by monitoring the plasmonic properties of the catalyst over time during the reaction [28]. On the contrary, other authors have presented proofs for the leaching of NP's atoms or ions (homogeneous catalysis) during the course of the reaction for catalysed C – C cross coupling reactions [29]. NPs prepared in the presence of dendrimers as stabilizers/template, referred to as dendrimer-encapsulated/stabilized NPs (DENS/DSNs) are generally very stable for longer periods of time in the absence of oxygen. Au-DENS in particular, have an advantage over other transition metal NPs in that they are very stable for longer time even when exposed to oxygen as compared to other metals such as Cu, Ru or Pt that easily gets oxidized on exposure to oxygen. Moreover, unlike other ligands or polymers that are used for NPs stabilization, the dendrimer template does not cause any steric effect around the encapsulated/stabilized catalyst's surface [8]. In the present study, we report a promising way of recycling these DENS catalysts through the use of dialysis membranes. This catalyst recycling method was first employed to dendrimer based catalysts by Van Leeuwen and Van Koten and their co-workers [30]. Gaab et al. reported the recyclability of dendrimer immobilized Cu(II)-based Lewis acid catalysts by making use of a dialysis membrane "bag" [31]. These catalysts were found to have superior selectivity and activity after a number of reaction cycles. These two systems however, consist of covalently bound homogeneous catalysts.

Based on that the size of the dendrimer used for this study, i.e. ~4.9 nm, and the assumption that most of the formed NPs are encapsulated within the dendrimers cavities, it should therefore not be possible for these DENS to diffuse out of the membrane to the outside reaction mixture unless leaching occurs. Only the small molecules of the reactants (NaBH_4 and 4-NP) can diffuse in and out of the dialysis membrane pores during the reaction. The driving force for this process may be a difference in pressure, concentration or in electrical potential. By employing this potentially simple, cost-effective and "greener" method for Au-DENS catalysed reduction of 4-NP we were able to provide additional answers to the question whether this reaction follows a homogeneous or heterogeneous type mechanism. This study proves unambiguously that the reduction of 4-NP is a heterogeneous process and not catalysed by dissolved metal atoms or "super small" clusters.

2. Experimental

2.1. Synthesis of Au-DENS

The synthesis of Au-DENS in this study was carried out as described in the literature [32]. The synthesis is generally carried out by adding metal ions to the aqueous dendrimer solution. The metal ions coordinate with the tertiary amine groups within the dendrimer structure. The addition of an excess reducing agent (e.g. NaBH_4) results in the nucleation of the coordinated ions to form NPs encapsulated within the dendrimer framework. Au_n -DENS prepared using the dendrimer:metal molar ratio of 1:13 and 1:100 are denoted as Au_{13} -DENS and Au_{100} -DENS respectively for this study and does not necessarily represent the actual number of atoms per nanoparticle.

2.2. Catalytic study

The catalyst was purified using a membrane bag prior the catalytic reactions. This was necessary in order to get rid of agglomerates or free or "super-small" Au NPs that are not encapsulated or stabilized by the dendrimer template. Therefore the participation of free Au NPs during the catalytic reaction is ruled out. The purified Au-DENS catalyst was then transferred into a new membrane bag for catalytic reaction. Au-DENS catalyst inside a dialysis membrane bag (10 μM , 5 mL) was placed in a conical flask (Fig. 3). De-ionised water, NaBH_4 and 4-NP were all added around the membrane sack in the flask and allowed to stir. Stirring process was important for speeding up the diffusion of the reactants into the membrane bag. Reaction solution was sampled at 1 h interval and the change in absorbance at λ 400 nm was monitored by a UV-vis spectrophotometer. Each single reaction cycle was run for 5 h. The membrane bag enclosed catalyst was purified for 1.5 h through dialysis before each reaction cycle commenced. This purification was necessary in order to remove some reaction products inside the membrane bag enclosed catalyst. The reaction products were extracted into organic phase using hexane solvent and then analysed with GC-MS (Shimadzu) (see Supplementary information for details).

3. Results and discussion

3.1. Characterization of Au-DENS

The synthesis of Au-DENS catalyst was monitored by a UV-vis spectrophotometer. HRTEM, EDX UV-vis were all used to characterize the prepared Au-DEN catalysts.

Fig. 1 illustrates all absorption spectra involved during the synthesis of Au-DENS. Aqueous dendrimer solution shows a weak absorption band around λ 280 nm (spectrum d). At higher dendrimer concentration, this band is more apparent. This band has also been reported to be pH dependent [33]. The addition of HAuCl_4 to the aqueous dendrimer solution resulted in the strong absorption and a shoulder band at λ 290 nm (spectrum c). This band is attributed to the charge transfer between the metal and the chloride ligands, i.e. ligand-to-metal-charge-transfer (LMCT). After the reduction of the dendrimer/metal ion complex with excess NaBH_4 , the peak at λ 290 nm disappeared, indicating a complete reduction of Au^{3+} metal ions coordinated within the dendrimer cavities to form Au-DENS. The formed Au-DENS gave rise to a new absorption band at λ 280 nm as well as a broad band around λ

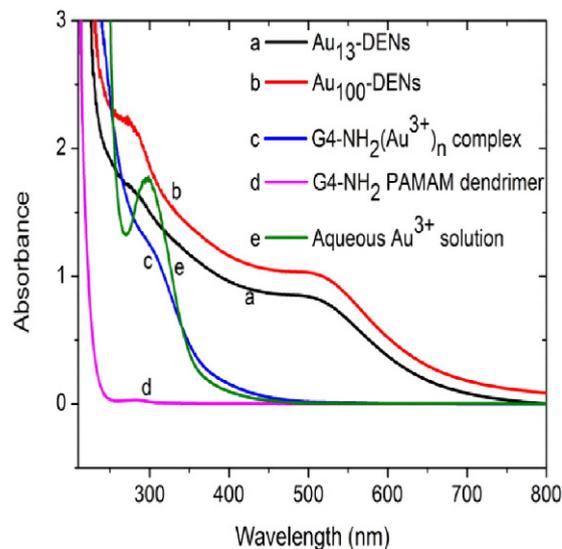


Fig. 1. UV-vis spectra of aqueous solutions of: (a) Au_{13} -DENS, (b) Au_{100} -DENS, (c) Au^{3+} /dendrimer complex, (d) aqueous dendrimer solution [10 μM] and (e) aqueous Au^{3+} solution [1 mM].

Download English Version:

<https://daneshyari.com/en/article/49692>

Download Persian Version:

<https://daneshyari.com/article/49692>

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