



Catalytic activity of palladium and gold dendrimer-encapsulated nanoparticles for methylene blue reduction: A kinetic analysis

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ABSTRACT

A kinetic analysis of the catalytic reduction of methylene blue (MB) by sodium borohydride (BH_4^-) using colloidal dendrimer-encapsulated palladium (Pd) and gold (Au) nanoparticles (PdDENS and AuDENS) is presented. The nanoparticles were prepared by the template method using generation 4 (G4) and generation 5 (G5) hydroxyl-terminated poly (amido)amine (PAMAM-OH) dendrimers for PdDENS and amine-terminated poly (amido)amine (PAMAM-NH₂) for AuDENS in aqueous solution. The catalysts were characterized by UV/vis spectrophotometry and transmission electron microscopy (TEM). The sizes of the particles obtained ranged from 1.3 to 2.3 nm with volume normalized surface areas between 0.02 and 0.06 m² L⁻¹. The reduction of MB by BH_4^- was monitored by UV/vis spectrophotometry using the stopped-flow technique and the kinetic data obtained was modeled to the Langmuir–Hinshelwood mechanism. The apparent rate constant for the reduction is related to the surface area *S* of the nanoparticles, the adsorption constants of MB (K_{MB}) and BH_4^- ($K_{\text{BH}_4^-}$) as well as to the kinetic constant *k* which is related to the rate-determining step of the reaction. The kinetic constant *k* was largest for PdDENS with the largest volume normalized surface area of 0.06 m² L⁻¹. K_{MB} values were 10 times larger than those of $K_{\text{BH}_4^-}$ in the case of PdDENS. The activation energy was lowest for the most catalytic active PdDENS at 34.5 ± 1.5 kJ mol⁻¹ as compared to 71.3 ± 1.6 kJ mol⁻¹, for the least active AuDEN catalyst.

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1. Introduction

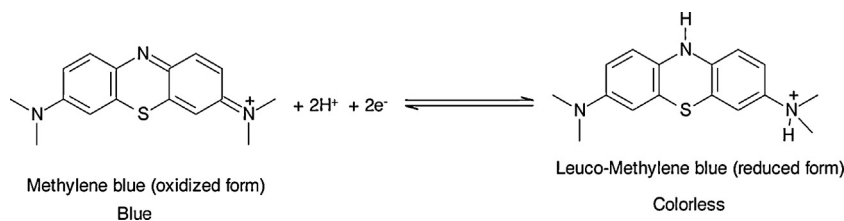
Catalysis of various chemical reactions using metal nanoparticles (NPs) in aqueous solution is an important area of research currently [1]. Transition metals such as palladium, gold or platinum have been used in many catalytic reactions including reduction [2–7], oxidation [8–10] and C–C coupling reactions [11–13]. An ideal redox catalyst relays electrons from the donor to an acceptor; hence the catalyst should have a reduction potential that is roughly between the values of the donor and an acceptor [14]. Some of the important features of the NPs that need to be considered are their size and shape as these have an effect on the catalytic activity of the NPs [15,16]. The metal nanoparticles are usually prepared in the presence of a stabilizer to prevent agglomeration and control the size of the particles [1]. Dendrimers [17] have in the last decade received a lot of attention as NP stabilizers as demonstrated by the extensive work on dendrimer-encapsulated NP (DENS) reported by the Crooks group [18–27] as well as by other

research groups around the world [28–33]. The branched and three-dimensional nature of dendrimer macromolecules [17] allows for the preparation of well-defined monodisperse nanoparticles, while not restricting the diffusion of reactants to the metal surface. These DENS have been used in the catalysis of various reactions and their catalytic activity evaluated in terms of kinetics and thermodynamics.

The Langmuir–Hinshelwood approach has been used to describe the mechanism of catalytic reactions [33–36]. The mechanism assumes that both reactants are first adsorbed on the surface of the catalyst prior to the reaction. On adsorption to the nanoparticle surface the BH_4^- transfers electrons to the metal. These are subsequently relayed to the adsorbed MB leading to its reduction. The rate-determining step for the reaction is, therefore, given by both adsorbed reactants. In studying the kinetics of such reactions it is important to fit the experimental data with the theoretical equations to ascertain whether the reaction mechanism conforms to the proposed model.

In this investigation two different sized dendrimer-encapsulated palladium nanoparticle (PdDENS) catalysts, stabilized by hydroxyl-terminated poly (amido)amine-G5-dendrimer (PAMAM-OH) as well as AuDENS stabilized by amine-terminated

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Scheme 1. Schematic representation of the reduction of methylene blue (MB).

PAMAM, were prepared in aqueous solution. The catalytic activity of the prepared DENs was evaluated using the reduction of the dye methylene blue (MB) by sodium borohydride, as a model reaction. The dye is blue in aqueous solution and is reduced by NaBH₄ to the colorless leuco-methylene blue form as shown in Scheme 1 [2].

The dye has a maximum absorption (λ_{max}) around $\lambda = 665$ nm in its oxidized form and its reduction can be monitored by observing the decrease in absorbance at this wavelength using UV–vis spectrophotometry. While the catalytic reduction of MB using Ag NPs [5], Pd NPs [6] and different metal nanoparticles (including Pd and Au) has been reported previously, none of these reports give a detailed kinetic analysis of the reaction.

2. Materials and methods

2.1. Materials and equipment

Generation four and five hydroxyl- and amine-terminated poly (amido)amine (G-4 and G-5 PAMAM-OH; 5 wt% in MeOH and PAMAM-NH₂; 10 wt% in MeOH) dendrimers, potassium tetrachloropalladate(II) (K₂PdCl₄), gold(III) chloride (HAuCl₄) and sodium borohydride (NaBH₄) were all purchased from Sigma–Aldrich. Sodium carbonate (Na₂CO₃), sodium hydrogen carbonate (NaHCO₃), sodium hydroxide (NaOH) and methylene blue (MB) were purchased from Merck Chemicals. The methanol in all the dendrimer solutions was removed *in vacuo* before use while all the other chemicals were used without further purification. All solutions were prepared in Milli-Q (18.3 M Ω cm) water. Ultraviolet–visible (UV–vis) spectra were measured in a Shimadzu UV-1800 Spectrophotometer connected to a Shimadzu CPS-Temperature Controller. High-resolution transmission electron microscopy (HRTEM) was performed on a JEOL JEM-2100F electron microscope with an accelerating voltage of 200 kV. The catalytic reduction of MB was investigated using a Hi-Tech Stopped-flow set-up consisting of Thermo-Scientific Haake SC100 for temperature control, a Sample Handling Unit (N₂ pressure 0.5 MPa), a CU-61 Control Unit (294.4 V), an SSU-60 Stepper Support Unit, a PS-678 Lamp Power Supply (Xenon) and a M300 Monochromator.

2.2. Catalyst preparation

2.2.1. Synthesis of Pd catalysts

Palladium DENs were prepared using a method reported in literature [20]. In brief the catalysts were prepared as follows; methanol of the dendrimer solution (G-4 PAMAM-OH for Pd₁₃ and G-5 PAMAM-OH for Pd₅₅) was removed *in vacuo* and the dry dendrimer diluted with Milli-Q water to give a 10 μ M solution. The catalysts were prepared by taking a 13-fold (Pd₁₃DENs) and a 55-fold (Pd₅₅DENs) molar excess of PdCl₄²⁻ to the dendrimer solution. The solution was stirred under inert conditions for 30 min. This was followed by the drop-wise addition of a 10-fold molar excess of NaBH₄ (0.10 M) solution to reduce the metal ions to zerovalent metal nanoparticles. The solution immediately turned brown, indicating the formation of the zerovalent metal particles.

2.2.2. Synthesis of Au catalysts

Gold DENs were prepared using a method reported in literature [21]. In brief the catalysts were prepared as follows; methanol of the dendrimer solution (G-4 PAMAM-NH₂ for Au₁₃ and G-5 PAMAM-NH₂ for Pd₅₅) was removed *in vacuo* and the dry dendrimer diluted with Milli-Q water to give a 10 μ M solution. The catalysts were prepared by taking a 13-fold (Au₁₃DENs) and a 55-fold (Au₅₅DENs) molar excess of AuCl₄⁻ to the respective dendrimer solution. The solution was stirred under inert conditions for 30 min. This was followed by the drop-wise addition of a 10-fold molar excess of NaBH₄ (0.10 M) solution prepared in 0.3 M NaOH. The solution immediately turned red-brown, indicating the formation of the zerovalent metal particles. The resulting nanoparticle colloidal suspensions were stirred at room temperature until use.

2.3. Catalytic reduction of MB

Both MB and NaBH₄ solutions were prepared in a buffer solution of pH 9.5 (prepared by mixing equal volumes of 0.02 M NaHCO₃ and Na₂CO₃). The stopped-flow sample handling unit was thoroughly cleaned with Milli-Q water and then by the buffer solution prior to use. In a typical catalytic run, the instrument was first blanked with the buffer solution, and then MB solution added using a one milliliter syringe into one injection port while NaBH₄ into which the catalyst suspension was added was placed into the second injection port of the stopped-flow instrument. The instrument was set to the Diode Array Mode with a dead time of 5 s. Equal volumes of the two solutions were then shot into the reactor for each run and the absorption spectrum taken at intervals of 0.05 s for 100 s or 500 s or until the reaction was complete as seen by zero absorbance at $\lambda = 665$ nm. Different sets of runs were performed in which catalyst loading (0.5×10^{-9} M to 5.0×10^{-9} M), MB (2.0×10^{-5} M to 6.0×10^{-5} M) and NaBH₄ (2.0×10^{-3} M to 2.5×10^{-2} M) concentrations as well as temperature (7–20 °C) were varied. Each run was performed in triplicate. Rate constants for the catalytic runs were calculated using the Kinetic Studio software.

3. Results and discussion

3.1. Preparation and characterization of Pd and Au DENs

Dendrimers were used as a template in the preparation of well-defined nanoparticles. Their branched nature allows for size and shape control, resulting in particles with a small diameter. The channels formed by the branches allow for the substrate to freely diffuse to the nanoparticle surface and also allow the products to diffuse away. UV–vis spectrophotometric analysis confirmed the formation of metal nanoparticles. In the case of palladium (Fig. 1a), a band at $\lambda = 208$ nm appears after the addition of Pd²⁺ to the dendrimer solution due to ligand-to-metal charge transfer (LMCT) which corresponds to the complexation of Pd²⁺ ions to the tertiary amines of the dendrimer interior [20]. The addition of reducing agent results in the disappearance of the LMCT band confirming the reduction of Pd²⁺ to zerovalent Pd. For AuDEN synthesis, the LMCT band which appears after addition of AuCl₄⁻ solution at λ

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