



Silver nanoparticles stabilized by a polyaminocyclodextrin as catalysts for the reduction of nitroaromatic compounds



Marco Russo, Francesco Armetta, Serena Riela, Delia Chillura Martino, Paolo Lo Meo*, Renato Noto

Università degli Studi di Palermo, Dip. STEBICEF—V.le delle Scienze, Parco d'Orleans, Ed. 17., 90128 Palermo, Italy

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ABSTRACT

Silver nanoparticles stabilized by means of *poly*-(6-*N,N*-dimethyl-propylenediamino)-(6-deoxy)- β -cyclodextrin were synthesized, characterized by different techniques (UV–vis spectroscopy, Dynamic Light Scattering, High Resolution Transmission Electron Microscopy, Fourier-transform IR Spectroscopy) and used as catalysts for the reduction of various nitrobenzene derivatives with sodium borohydride. The nanocomposites obtained appear to have an organized structure, with a metal core surrounded by a layer-structured coating shell. Kinetic data, rationalized in terms of a modified Langmuir–Hinshelwood model, evidenced a non-linear dependence of the reaction rate on the concentration of the catalyst. This was explained on the grounds of the catalytic activity of differently covered catalyst areas. Careful analysis of kinetic data, in particular the effect of the *para* substituent on the nitroarene structure and the trends of the induction period observed at the beginning of the reaction, provided with interesting insights on the reaction course, and brought us to critically reconsider several mechanistic ideas reported in previous literature.

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1. Introduction

The reduction of aromatic nitrocompounds is an important synthetic route leading, under the proper reaction conditions, to different nitrogen-containing derivatives [1]. In particular, the reduction to anilines (Scheme 1), which has also a great interest as an industrial process, is generally carried out with strong reducing agents or under harsh conditions. The most common protocols provide the use of LiAlH_4 , transition metals in strongly acidic media (Fe and conc. HCl is a typical industrial method), or catalytic hydrogenation.

Unfortunately, these conditions may be unsuitable whenever particularly delicate functional groups are present in the molecule. Therefore, the availability of milder alternative methods has an undoubted appeal. In this context, the use of NaBH_4 in the presence of noble metal nanoparticles (NPs) has attracted a certain interest [2,3]. The reduction of 4-nitrophenol or 4-nitroaniline (to 4-aminophenol and 1,4-diaminobenzene respectively) has been successfully carried out using NPs stabilized by various capping agents, including biopolymers such as dextran [4,5] or alginate

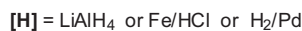
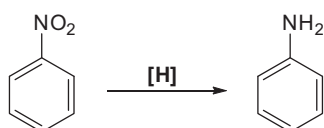
[6–8], and PAMAM- or PPI-type dendrimers [3,9,10]. The latter class of auxiliaries is particularly interesting, because dendrimers provide a strictly defined micro-environment for the formation of the NP and for the actual nitroarene reduction process as well.

Cyclodextrins (CDs), both native or chemically modified with suitable donor groups, constitute a class of alternative capping agents for the formation of metal NPs which have been occasionally employed [11,12]. The most known example is probably constituted by the *heptakis*-(6-thiol)-(6-deoxy)- β CD [13], which has been successfully used for the synthesis of Au or Ag NPs. Recently, some of us synthesized a new class of polyaminocyclodextrin products [14], which have been tested as effective auxiliary agents for the preparation of Ag nanoparticles. The CD derivatives were obtained by a simple nucleophilic displacement reaction between the *heptakis*-(6-iodo)-(6-deoxy)- β CD and various polyamines (Scheme 2).

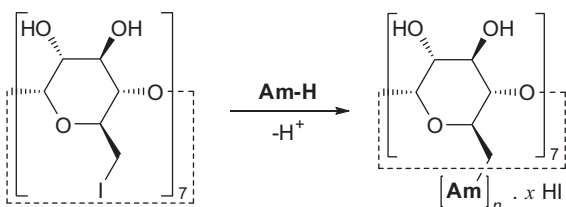
However, due to the unavoidable occurrence of poly-substitution, the reaction affords mixtures of products bearing a different number of polyamino pendants [15]. As a matter of fact, the same polyamine unit may substitute more than one iodine on the same CD scaffold. The obtained materials, which are isolated as partial hydroiodides, have been fully characterized by means of Nuclear Magnetic Resonance, Electrospray Ionization Mass Spectrometry and potentiometric titration. The combined use of these

* Corresponding author.

E-mail address: paolo.lomeo@unipa.it (P.L. Meo).



Scheme 1. Reduction of nitrobenzene to nitroaniline.



Scheme 2. Synthesis of polyamino CDs.

techniques allowed to identify the different constituents of the mixtures, to determine the average number of polyamine pendants (n) and formal HI molecules (x) per CD unit, and to calculate the possible protonation or charge status as a function of the pH.

Despite the nitroarene reduction catalyzed by metal NPs has been known for relatively long time, the actual mechanism of catalysis has not been satisfactorily understood, and even the kinetic features of the process are still debated. There is no general agreement about the kinetic order of the reaction, which is usually reported as first order in the nitroarene [3,6,10,12,16–18], but which has been also occasionally described as zeroth order [2,8]. Moreover, the possibility to apply this reaction to further nitroarene derivatives has never been explored in detail. Therefore, a systematic investigation and in general a critical reconsideration of the entire topic seemed interesting. In this context, we reasoned that the use of a cyclodextrin-capped Ag-NP system as the catalyst could be particularly intriguing. Indeed, CDs as auxiliary agents may provide both a suitable micro-environment for the formation and the stabilization of the NP, and a sort of receptor site on the catalyst surface, constituted by the CD cavity, able to bind and direct the nitroarene substrate.

In the present work we investigated the reduction reaction of various nitroarene derivatives **1–8** (Fig. 1) with NaBH_4 in the presence of two Ag-NP catalyst systems, obtained by using the *poly*-(6-*N,N*-dimethyl-propylenediamino)-(6-deoxy)- β CD (**AmCD**, Fig. 2) as the capping agent.

The structural and morphological characterization of the Ag-NP systems chosen as catalysts was performed by means of combined UV-vis spectroscopy, Dynamic Light Scattering (DLS), High Resolution Transmission Electron Microscopy (HR-TEM) and FT-IR spectroscopy. These techniques allowed to get information on the size and polydispersity of the NP suspensions, as well as to

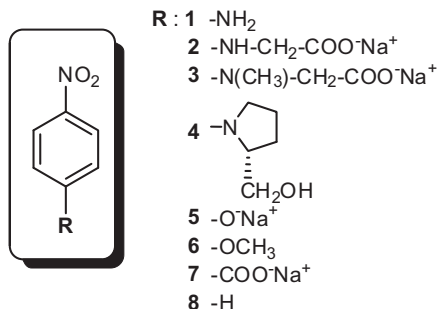


Fig. 2. Structure of AmCD.

investigate the morphology of the NPs. The chosen nitroarene substrates differ for the substituent at the *para* position with respect to the reactant nitro group. They were suitably selected to present significant variations in their molecular properties [19,20]. In

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