



Review

Basic concepts and recent advances in nitrophenol reduction by gold- and other transition metal nanoparticles



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ABSTRACT

This review presents the basic concepts and recent developments and advances of gold nanoparticle (AuNP)-catalyzed 4-nitrophenol (4-NP) reduction to 4-aminophenol (4-AP) by sodium borohydride, including the catalytic mechanism, the variety of stabilizers, and dendritic, natural and heterogeneous AuNP supports. The nano-gold catalysts are classified according to different stabilizers, the review contains 205 citations.

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1. Introduction

Since the seminal work by Haruta [1], gold nanoparticles (AuNPs) have been considered as excellent catalysts even at low temperature, which is in complete contrast with bulk or even microscopic gold that has a long standing reputation of being an inert metal [2–4]. Among the many reactions that are catalyzed by AuNPs, the reduction of nitro derivatives stands as a major challenge because of the pollutant nature of these compounds [5]. The reduction of 4-nitrophenol (4-NP) and other nitroaromatics is particularly crucial, because these compounds are anthropogenic, toxic and inhibitory in nature. The 4-NP reduction product, 4-aminophenol (4-AP), finds applications as a photographic developer of black and white films, corrosion inhibitor, drying agent, precursor for the manufacture of analgesic and antipyretic drugs, and in particular is an important intermediate in the synthesis of paracetamol [6–8].

Moreover, 4-NP reduction by NaBH₄ is a “model catalytic reaction” [9]. Such a reaction should be well controlled yielding a single product from a single reactant at mild temperatures, and it should not proceed in the absence of the catalyst. The 4-NP reduction proceeds in water at room temperature in which the reactants and AuNP catalysts are often soluble, and the catalyst is stable during the reaction [9]. This reaction was first reported in 2002 by the groups of Pal [10] and Esumi [11] who disclosed these features that have further been used by a large number of researchers as a test reaction to evaluate the catalytic properties of various AuNPs [6] and for electrochemical biosensing (vide infra, Section 3.3).

The common and most efficient way for the reduction of 4-NP is to introduce NaBH₄ as a reductant and a metal catalyst such as AuNPs [12], AgNPs [13], PdNPs [14], PtNPs [15] and NiNPs [16]. Compared with other metal catalysts, AuNPs have two unique properties: (i) the catalytic activity of gold is directly related to the particle size, and the catalytic activity is only observed at the nanometric scale but not micrometric scale; (ii) Au catalysts are active under mild conditions, even at ambient temperature or less. However, in some reactions, “naked” AuNPs do not function as catalysts, thus a real challenge in the design of an active and selective nanogold catalysts is the choice of the appropriate stabilizer in terms of its AuNP affinity, stabilization ability and large surface area [8,9,17,18]. Recently, a variety of AuNP ligands have been compared, and the results were that triazoles gave faster kinetics than thiolate and citrate and that polymer, and especially dendritic ligand backbones, slowed down the reaction [19]. Small particles most often have a high activity compared with relatively large particles, because the proportion of active surface gold atoms vs. the total number of gold atoms in a AuNP is all the higher as the AuNP is smaller, but exceptions have also been reported (vide infra, Section 3.1).

2. Reaction mechanism

The 4-NP reduction by NaBH₄ in water catalyzed by AuNPs reaction is easily monitored by UV–vis spectroscopy, and the decrease of

the strong absorption of 4-NP at 400 nm is treated in terms of a first-order reaction in the presence of excess NaBH₄. The variation of this decay rate is currently used to compare various AuNP catalysts. The diffusion of the reactants is fast compared with the rate-limiting step at the AuNP surface. This was deduced from the fact that the *second Damköhler number (Dall)* that is the ratio between the reaction rate and the diffusion rate for a first-order reaction is much smaller than unity for this reaction:

$$Dall = k/\beta a \ll 1$$

where k is the reaction rate constant, β is the mass transport coefficient, and a is the AuNP surface area. The coefficient β is the diffusion coefficient divided by the length scale over which the reaction takes place. *Dall* is of the order of 10⁻³ for the AuNP-catalyzed 4-NP reduction by NaBH₄ [9].

Temperature change does not provoke a change in mechanism in a suitable temperature range, thus the activation energy, E_A , can be easily derived from the respective Arrhenius plots (vide infra, Section 2). These properties make this reaction as close as possible to the definition of a so-called “model” reaction, although some restrictions or approximations have been reported (vide infra). The stability of the AuNPs during the catalytic 4-NP reduction and the resulting determination of the activation energy, E_A allows investigating the influences of the AuNP size and shape on the reaction. Ballauff and his group have shown that the kinetics of this model reaction can be treated in terms of the Langmuir–Hinshelwood (LH) model [20]: both reactants adsorb on the surface of the particles before the reaction. The adsorption of both substrates is fast, and it is modeled in terms of an equilibrium process described by a Langmuir isotherm. The adsorbed species then react, and finally the reaction product dissociates from the surface. This model gave a correct description of the kinetics of the reaction [20]. In particular, the rate constant decreases with increasing the 4-NP concentration and reaches a maximum upon increasing the NaBH₄ concentration, indicating according to the LH model a competition of the two reactants for AuNP surface adsorption sites. The data provide the thermodynamics adsorption constants K_{4-NP} and $K_{BH_4^-}$ and the rate constant of the reaction at the AuNP surface. In addition, the reaction usually only starts after an induction time t_0 that has been taken into account by Zhou et al. by the restructuring of the AuNP surface by the reactants [21]. Here the borohydride reacts with the AuNP surface to reversibly give Au–H bonds [20,22], and the reaction between the Au–H bonds and the adsorbed 4-NP to give 4-AP is the rate-limiting step (i.e. the diffusion and adsorption of the reactants as the desorption are fast compared with the reaction on the AuNP surface) [9,20]. The rate constant k is proportional to the AuNP surface S in the LH model:

$$dc/dt = -kc = -k_1cS; \quad c = 4-NP \text{ concentration}$$

Thus according to the LH model, k_1 is independent of the AuNP surface, but it reflects both the adsorption of the substrate (K_{4-NP} and $K_{BH_4^-}$) and the reaction rate at the AuNP surface itself [9,23].

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