



Highly efficient and selective reduction of nitroarenes into anilines catalyzed by gold nanoparticles incarcerated in a nanoporous polymer matrix: Role of the polymeric support and insight into the reaction mechanism



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ABSTRACT

Gold nanoparticles supported onto a nanoporous semicrystalline polymorphic polymer matrix consisting of syndiotactic polystyrene-co-cis-1,4-polybutadiene multiblock copolymer (AuNPs-sPSB) were investigated as catalyst in the reduction of nitroarenes into anilines using sodium borohydride as reductant. The crystalline phase and the morphology of the polymeric support were varied to assess their influence on the selectivity of the reaction pathway. The β and γ crystalline forms, which are not permeable to small molecules, led to a partial reduction of nitrobenzene into both azoxybenzene and diazobenzene whereas the porous δ and ϵ crystalline forms efficiently catalyze the complete reduction into aniline through the *condensation route* of the reaction mechanism proposed by Haber, achieving the highest activities reported so far for this reaction.

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1. Introduction

Gold nanoparticles (AuNPs) stabilized by inorganic supports or embedded into polymer matrices are emerging as a powerful tool in sustainable catalysis. Following the pioneering studies of Haruta on the low temperature oxidation of carbon monoxide to carbon dioxide catalyzed by AuNPs supported onto transition metal oxides using dioxygen as oxidant, a variety of aerobic oxidation reactions have been successfully carried out under very mild conditions and with high efficiency and selectivity [1]. The reaction mechanism is

Abbreviations: AAS, atomic absorption spectroscopy; AB, azobenzene; AN, aniline; AOB, azoxybenzene; AuNPs, gold nanoparticles; BET, Brunauer–Emmett–Teller method; ICP-OES, inductively coupled plasma optical emission spectrometry; NB, nitrobenzene; SEM, scanning electron microscopy; sPSB, syndiotactic polystyrene-cis-1,4-polybutadiene multiblock copolymer; SAED, selected area electron diffraction; TEM, transmission electron microscopy; WAXD, powder wide angle X-ray diffraction.

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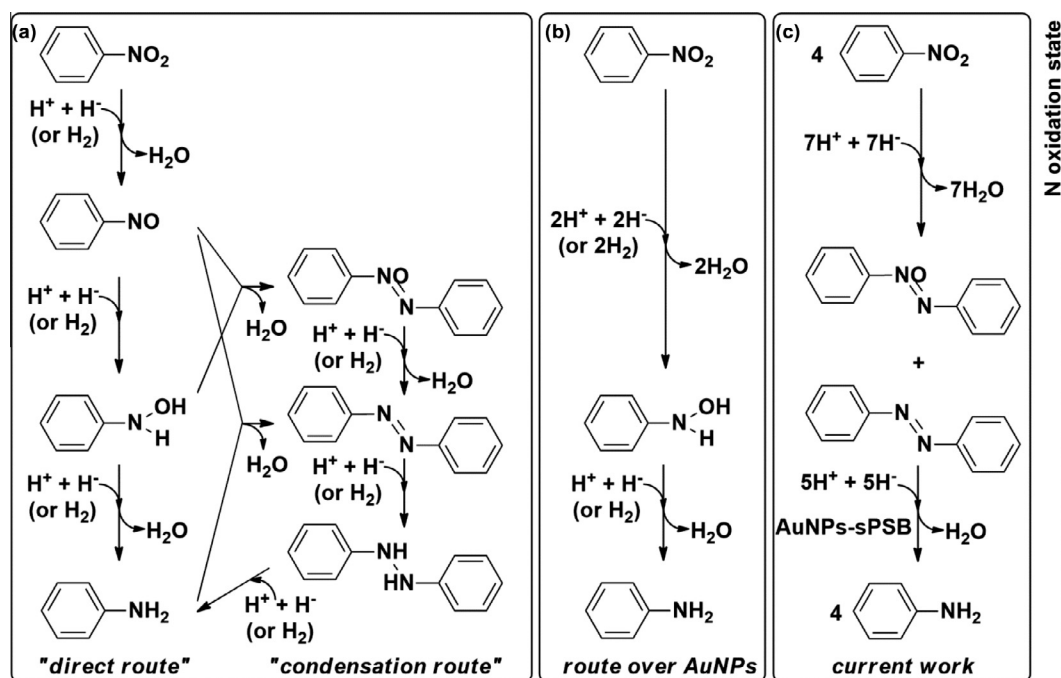
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currently matter of debate, but some features seem, to date, well assessed and commonly accepted [1e,2]. A hydride shift from the substrate to be oxidized to the surface of the AuNPs produces the Au–H species that initiates the specific cascade of reactions leading to the oxidation of the targeted molecule: this reaction is considered the rate determining step, as extensively demonstrated by isotope kinetic measurement, EPR spectroscopy of the catalyst solution under aerobic conditions, and Hammett plots [2a,f,3]. DFT calculations substantiated this reaction pathway, initially proposed on the basis of a number of experimental evidences [2b,f,4]. Actually labeling experiments using [18] O₂ showed no incorporation of the isotopomer in the oxidation products to confirm that dioxygen acts just as hydride scavenger from the AuNPs surface to produce the hydroperoxo species, Au–OOH, that in turn decomposes to hydrogen peroxide by protonolysis [5]. Interestingly the possibility of obtaining stable Au–H intermediate species paved the way to gold catalysts suitable for reduction reactions. Corma et al. first showed that AuNPs supported onto TiO₂ or Fe₂O₃ allow reduction of nitroaromatics into the corresponding anilines using molecular dihydrogen under



Scheme 1. (a) Reaction mechanism for noble metal catalyzed NB reduction proposed by Haber; (b) reaction pathway proposed for AuNPs with H_2 or NaBH_4 as reducing agent; (c) reaction pathway identified in the current work.

harsh conditions (100–130 °C, 10–25 bars of H_2 , 1–9 h) [6]. The chemoselective hydrogenation of nitroaromatics comprising reducible functional groups, as e.g. nitrostyrene, nitrobenzaldehydes and nitrobenzonitriles, was thus successfully accomplished. Other authors showed later that the reaction could be carried out under milder conditions using alternative and more efficient reductants as the ammonia-borane complex [7], sodium borohydride [8], isopropanol [9], silanes [10], $\text{CO}/\text{H}_2\text{O}$ [11] (WGS reaction as source of dihydrogen). Intriguingly UV–Vis light irradiation of the AuNPs – TiO_2 catalysts produced the selective reduction of nitrobenzenes to azobenzenes [12].

AuNPs seem to mimic biological enzymes, namely nitroreductases, which catalyze the reduction of nitrocompounds using flavin mononucleotide (FMN) or flavin adenine dinucleotide (FAD) as prosthetic groups, and nicotinamide adenine dinucleotide (NADH) or nicotinamide adenine dinucleotide phosphate (NADPH) as hydride donors [13]. The sequential bi-electron transfer from NAD(P)H results into the formation of the nitroso and hydroxylamine derivatives, and finally of the primary amine [14]. The presence of the hydroxylamino intermediate is well-established and proven in a number of studies; on the contrary, nitrosobenzene is extremely reactive and its bi-electron reduction is so fast that this species cannot be isolated or detected. The cascade of reaction intermediates in the bioreduction of nitroaromatics is analogue to that proposed in the Haber mechanism as direct route catalyzed by noble metals (*vide infra*; Scheme 1).

We have recently reported that AuNPs embedded into a nanoporous crystalline polymer matrix consisting of the syndiotactic polystyrene-*cis*-1,4-polybutadiene multiblock copolymer (AuNPs-sPSB) efficiently catalyze the selective aerobic oxidation of primary and secondary allyl, and of benzyl and *benzyl like* alcohols, to the corresponding aldehydes and ketones, leaving alkyl alcohols not reacted [15]. These findings allowed the efficient and selective synthesis of alkyl cinnamates via the in situ aerobic oxidative esterification of cinnamyl alcohols with alkyl alcohols [16,17]. The polymer host matrix of AuNPs-sPSB mainly consists of syndiotactic polystyrene, a semicrystalline thermally stable and chemically

inert polymorphic polymer that exhibits five crystalline forms, namely α , β , γ , δ and ϵ [18]. While the α , β , γ polymer phases are poorly permeable to small organic molecules, the δ and ϵ crystalline forms are nanoporous and include, in the crystalline lattice, nanovoids and nanochannels respectively; a variety of halogenated and aromatic molecules can be therein hosted, producing co-crystals and intercalate structures, respectively [19]. The remarkable activity and selectivity of the AuNPs-sPSB catalyst in oxidation catalysis was attributed to the porosity of the ϵ form of the polymeric support which allows fast and selective diffusion of the reactants to the catalytic active sites [15,16]. These seminal and encouraging results prompted us to definitively demonstrate the effectiveness of this nanoporous host polymer matrix in other examples of redox reactions catalyzed by AuNPs. Considering that both nitrobenzenes [20] and azobenzenes [21] produce stable co-crystals with the δ and ϵ forms of syndiotactic polystyrene we decided to explore the reduction of nitroaromatics using the AuNPs-sPSB catalyst and NaBH_4 as reductant, aiming also to elucidate the reaction pathway.

2. Experimental section

2.1. General procedures and materials

The manipulation of air- and moisture-sensitive compounds was performed under nitrogen atmosphere using standard Schlenk techniques and a MBraun glovebox. Toluene (99.5%) was dried over calcium chloride, refluxed for 48 h over sodium and finally distilled before use in moisture- and oxygen-sensitive reactions. Tetrahydrofuran (99.5%) was dried over potassium hydroxide, refluxed for 48 h over Na/benzophenone and distilled before use in the synthesis of the catalyst. Styrene (99%) was purified by stirring for 12 h over calcium hydride before distillation under reduced pressure. Tetrachloroauric acid trihydrate ($\geq 49.0\%$ Au basis), sodium triethylborohydride (1.0 M in THF), water (HPLC grade), methanol (HPLC grade), ethanol ($\geq 99.8\%$), ethylene glycol ($\geq 99\%$),

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