

Article

Gold Nanoparticles Embedded in Poly(2,6-dimethyl-1,4-phenylene) Oxide Matrix: A Selective and Reusable Catalyst for Nitroarene Reduction via Polymer-Controlled Reaction Pathway

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Abstract

Gold nanoparticles (AuNPs) supported by a polymer matrix of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) were investigated as a catalyst for the selective reduction of nitroarenes (NAs) to aniline derivatives (ANs), using sodium borohydride (NaBH₄) as a reductant. A systematic investigation of reaction parameters, including temperature, solvent, and NaBH₄ concentration, revealed a strong influence on both catalytic activity and product selectivity. Under optimised conditions (80 °C for 60 min using a [Nitrobenzene]/[Au] molar ratio of 510), the AuNPs-PPO catalyst achieved quantitative conversion and excellent selectivity toward aniline (AN) (>99%), with turnover frequencies (TOF) up to 510 h^{−1}. Methanol (CH₃OH) was identified as the optimal solvent, while lower reductant concentrations led to the formation of intermediates such as azobenzene (AB), azoxybenzene (AOB), and hydrazobenzene (HB), providing insight into the reaction pathway. The catalyst exhibited remarkable recyclability over multiple runs without significant loss of activity or structural changes, as confirmed by Wide-angle X-ray diffraction (WAXD) analysis. Furthermore, the catalytic system proved effective for a range of substituted nitroarenes (SNAs), demonstrating broad substrate scope and functional group tolerance. These results highlight the potential of AuNPs-PPO as a versatile, selective, and sustainable platform for the reduction of NAs under mild and environmentally benign conditions.

Keywords: gold nanoparticles; porous polymer; nitroarene; reduction; heterogeneous catalysis; aniline



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1. Introduction

Nitroarenes (NAs) are widely used in numerous industrial sectors to produce dyes, explosives, herbicides, pesticides, pharmaceuticals, synthetic rubber, and phenolic resins [1]. Their extensive use entails significant risks for both the environment and human health [2]. NAs can penetrate aquatic systems and soil, causing persistent environmental contamination with negative effects on ecosystems [3]. Nitrobenzene (NB), for example, has been detected in surface waters, where it persists for a long time because of its chemical stability. From a biological perspective, NAs exhibit a complex toxicological profile. They are

reactive electrophiles, capable of forming secondary toxic metabolites or uncouplers of oxidative phosphorylation, interfering with cellular energy processes [4]. The liver, nervous system, and immune system are damaged by these chemicals to the point of producing mutagenicity and potential carcinogenicity [5]. Consequently, uncontrolled exposure to NAs represents a concrete concern for human health and environmental protection [6].

Reduction of NAs to the corresponding less toxic and degradable anilines (ANs) is one of the most promising strategies for environmental remediation and for synthesising nitrogen-containing compounds of interest in material design and drugs [7–12]. Although several methods have been developed over the years [13–18], the selective hydrogenation of NAs remains one of the most difficult challenges when other reducible functional groups are also present in the substrate skeleton. The traditional Béchamp method allows the industrial-scale reduction of NAs, but the stoichiometric amount of reducing metal in the presence of acids makes this approach unsustainable to date [19].

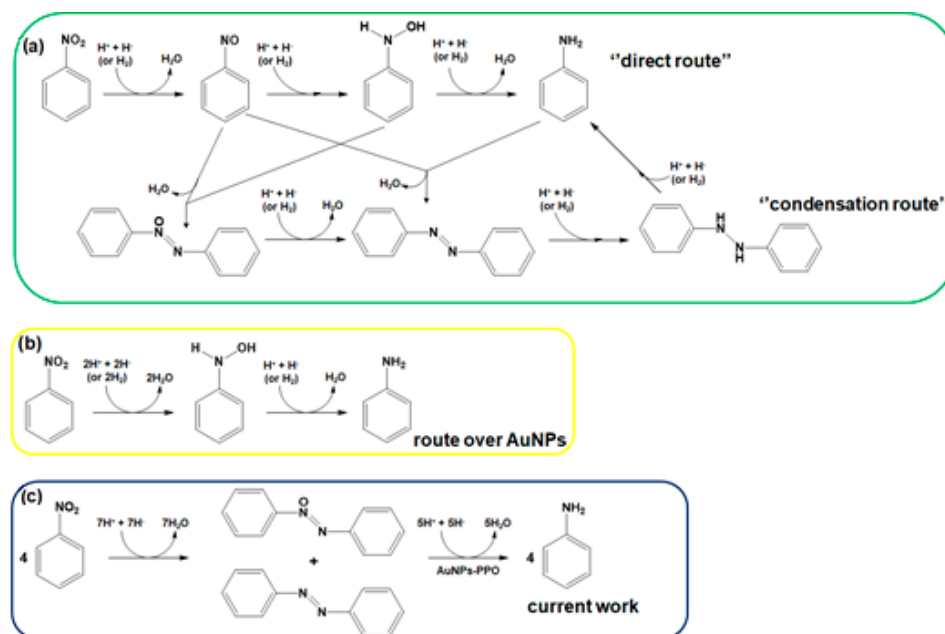
Supported gold nanoparticles (AuNPs) have recently attracted rapidly growing interest because of potential applicability in many reactions of both industrial and environmental relevance [20,21], such as alcohol oxidation [22–29], selective gas-phase hydrogenation of 1,3-butadiene to butane [30–32], chemoselective hydrogenation of unsaturated aldehydes [33], and selective hydrogenation of NAs [34]. In the latter topic, Qiu and co-workers reported the first chemoselective hydrogenation of chloronitroarenes into chloroanilines using AuNPs of 7.0–9.0 nm dispersed on silica at 140 °C and a H₂ pressure of 4.0 MPa [35]. AuNPs supported on zirconia [36] similarly led to chemoselective hydrogenation of chloronitroarenes without the formation of dechlorinated products [37–40]. The Au/TiO₂ catalyst resulted in highly efficient chemoselective hydrogenation of nitro derivatives: under optimised reaction conditions, conversions greater than 98% and selectivity greater than 90% were obtained [41].

Although the detailed mechanism of these transformations is still under study, some key aspects are now widely accepted. In particular, the formation of Au–H intermediate species plays a central role in initiating a cascade of reactions of the target molecule [42]. Interestingly, the possibility of stabilising these Au–H species has also opened new perspectives in gold-catalysed reduction reactions; this has allowed their use to extend from oxidation catalysts to effective promoters in reduction reactions as well [43].

Significant efforts have been devoted to the development of advanced AuNPs-based catalytic systems for NAs reduction, with particular emphasis on the control of nanoparticle size, stabilisation strategies, and the design of tailored support materials [44–46]. Recent examples include AuNPs confined or dispersed within porous organic frameworks, polymeric networks, and other functional matrices, where the surrounding environment can influence substrate accessibility, nanoparticle stability, and catalytic selectivity [47–52]. These studies have highlighted that the catalytic performance of AuNPs is not solely determined by the intrinsic properties of AuNPs, but also by the ability of the support to regulate metal dispersion and the interaction between reactants and active sites. Nevertheless, many highly active systems reported to date require sophisticated support architectures or multistep synthetic procedures, motivating the exploration of simpler and more accessible polymer-supported AuNP catalysts.

In this context, the present work reports the efficient reduction of various NAs using AuNPs trapped within a polymer matrix of poly(2,6-dimethyl-1,4-phenylene oxide) (AuNPs-PPO) [53]. PPO is an inexpensive, readily available polymer characterised by a nanoporous semicrystalline structure showing a high glass transition temperature ($T_g = 220$ °C) and remarkable thermal stability, which makes this polymer an ideal support for catalytic applications. The synthesis of AuNPs-PPO is simple and economical, allowing precise control of the incorporated gold catalyst and its dispersion onto the polymer

support. In this work, various reaction conditions and solvents were tested to study their influence on the selectivity of the process, aiming to avoid the formation of undesired by-products such as azobenzene (AB), azoxybenzene (AOB), and hydrazobenzene (HB) (Scheme 1) [54,55]. Among the different reducing agents explored for the conversion of NAs, sodium borohydride (NaBH_4) has been widely employed in combination with metal nanoparticle-based catalysts due to its ability to promote hydrogen transfer reactions on metal surfaces. Acting as an effective hydride source, NaBH_4 enables the selective reduction of nitro groups under relatively mild conditions [56,57]. In addition to its catalytic compatibility, NaBH_4 is attractive because of its low cost, commercial availability, ease of handling, and the formation of borate species as the main inorganic byproducts [58].



Scheme 1. (a) Proposed reaction pathway for noble metal-catalysed NB reduction according to Haber; (b) reaction pathway proposed for AuNPs-catalysed reduction using H_2 or NaBH_4 as reducing agents; (c) reaction pathway proposed for AuNPs-PPO-catalysed NB reduction based on the experimental observations of the present work.

In line with the principles of sustainable chemistry, this study aims to optimise the catalytic reduction through a critical analysis of both the operational conditions and the different morphologies of the catalyst, with the goal of achieving a balance between efficiency, selectivity, and low environmental impact.

2. Results

2.1. Synthesis and Characterisation of the AuNPs-PPO Catalyst

The AuNPs-PPO catalyst was synthesised following a recently developed procedure that allows the gold loading to be finely controlled at 2 wt% [59]. Briefly, the PPO support was suspended in THF, and $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was added as a gold precursor. Subsequent reduction with NaBHET_3 , followed by rapid precipitation of the polymer composite upon addition of a large excess of CH_3OH , afforded the AuNPs-PPO system. The actual gold content was determined by ICP-OES analysis after acidic mineralisation, confirming the expected Au loading.

The structural features of the catalyst were first investigated by WAXD analysis. The diffraction pattern shows the characteristic reflections of face-centred cubic Au(0), with the most intense contribution centred at $2\theta \approx 38^\circ$, corresponding to the Au(111)

plane (Figure 1a) [60]. The average crystallite size, estimated from the full width at half maximum of this reflection using the Scherrer equation, was approximately 5 nm. In addition, the broad diffraction profile observed in the 2θ range of $5\text{--}35^\circ$ is consistent with the amorphous nature of the PPO matrix (Figure 1a) [61,62]. XPS analysis previously reported for the same AuNPs-PPO system, supported by WAXD, HR-TEM, and CO-probed FT-IR spectroscopy, indicated the presence of predominantly metallic Au(0) nanoparticles with partially positively charged surface atoms, Au(0) δ^+ , arising from interactions with the PPO matrix. Accordingly, the Au $4f_{7/2}$ and Au $4f_{5/2}$ signals observed at approximately 84.0 and 87.8 eV, respectively, are consistent with this assignment rather than with appreciable amounts of Au(I) or Au(III) species [63,64].

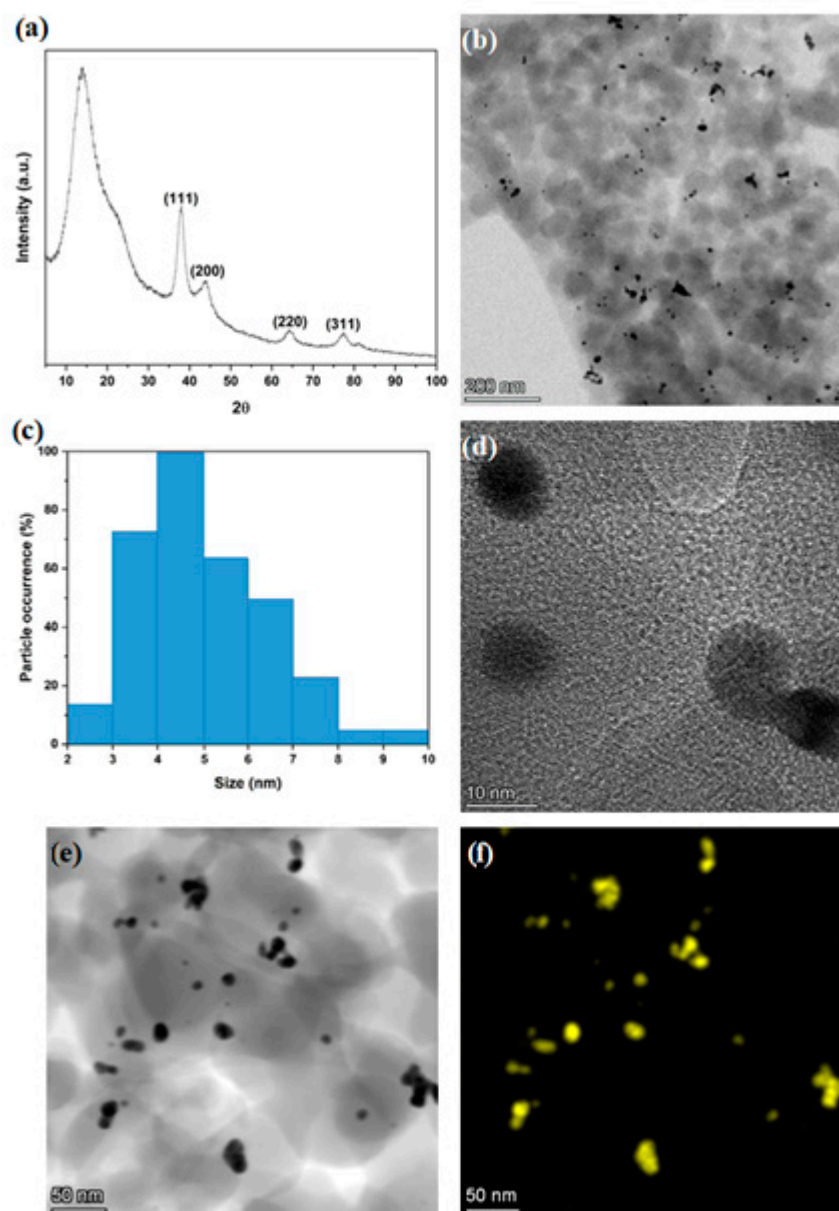


Figure 1. Characterisation of AuNPs-PPO: WAXD pattern (a); TEM micrograph (b) with the corresponding size distribution plot (c); HRTEM of nanoparticles (d); bright-field STEM image (e) with the corresponding EDX micrograph highlighting the gold distribution (f).

The adopted synthetic strategy promotes controlled nucleation and stabilisation of small AuNPs within the PPO matrix. TEM and HR-TEM analyses revealed small nanoparticles with dimensions in excellent agreement with the WAXD-derived crystallite size

(Figure 1b–d). The particles are predominantly spherical and mainly distributed in the 3–6 nm size range, with only limited local aggregation, as confirmed by the particle size distribution analysis (Figure 1c). STEM imaging combined with EDX mapping further confirmed the homogeneous distribution of gold throughout the polymeric support, while also evidencing the presence of small nanoparticle aggregates in selected regions (Figure 1e,f). The Au nanoparticles are not exclusively located on the external surface of the polymer, since the swelling of PPO in THF before reduction of the gold precursor favours nanoparticle nucleation and stabilisation throughout the polymer matrix. STEM-EDX analysis confirms the distribution of gold within the support, although limited local aggregation is observed in selected regions. The interaction between AuNPs and PPO is therefore better described as an interfacial electronic and confinement effect rather than as a well-defined coordination bond. In particular, the previously observed partial positive charge of surface Au atoms suggests that the polymer matrix affects the electronic density of the nanoparticle surface. However, the available data do not allow this interaction to be assigned exclusively to direct coordination between gold and the ether oxygen atoms of PPO. Furthermore, the native AuNPs-PPO catalyst showed a BET specific surface area of $30 \text{ m}^2 \cdot \text{g}^{-1}$, indicating the presence of accessible surface sites within the polymer-supported catalytic system.

The catalytic performance of AuNPs-PPO cannot be attributed to a single structural parameter, but rather to the combined effect of accessible metallic Au surface sites and the stabilizing environment provided by the PPO matrix. The polymer promotes the formation and preservation of small Au nanoparticles, limits extensive aggregation, and allows the reactants to reach the metal surface through its nanoporous structure. Although the measured BET surface area confirms the presence of accessible sites, surface area alone does not account for the observed catalytic behaviour. The activity and selectivity of the system therefore arise from the synergistic combination of metallic Au(0) sites, nanoscale dispersion, and confinement within the PPO matrix.

Overall, these characterisation data demonstrate that the PPO matrix acts as an effective stabilising environment for the formation of small metallic AuNPs, limiting extensive aggregation while preserving accessibility to the catalytic metal surface.

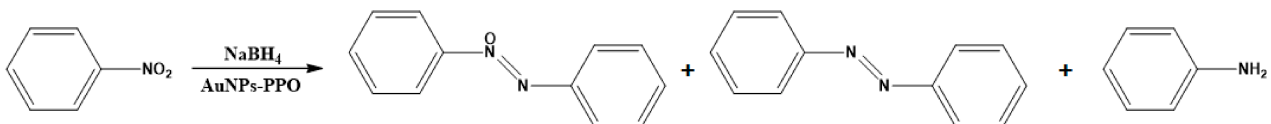
2.2. Reduction of NB Catalysed by AuNPs-PPO

ANs represent essential building blocks in fine and bulk chemical production. They are widely used in the synthesis of dyes and pigments, pharmaceuticals, agrochemicals, polymer precursors, explosives, and antifungal agents, owing to their versatile reactivity in electrophilic substitution reactions and their ability to coordinate transition-metal centres [65–68]. Conventional synthetic approaches to aromatic amines include Pd- or Ni-catalysed C–N cross-coupling reactions of aryl halides with ammonia or primary amines, typically requiring tailored ligands and bases. Alternatively, reductive amination of aromatic carbonyl compounds with ammonia or primary amines provides imine intermediates that can be reduced in situ using NaBH_4 or H_2/Pd systems [69–72]. The use of NaBH_4 enabled efficient reduction under the mild reaction conditions employed in this study, in agreement with its well-established ability to promote hydrogen-transfer reactions on Au surfaces [73–78]. Among the available routes, the catalytic reduction of NAs is particularly attractive because nitroaromatic substrates are readily available and the corresponding ANs can be obtained under relatively mild conditions. In this context, NaBH_4 is a convenient hydrogen source due to its low cost, ease of handling, and formation of relatively benign borate by-products. Moreover, NaBH_4 -mediated reductions are known to be efficiently promoted by noble-metal nanoparticles, including AuNP-based catalysts [73–78]. On this basis, the catalytic performance of AuNPs-PPO was investigated in the reduction of NB using NaBH_4 as a reducing agent. Preliminary experiments were performed in CH_3OH ,

which was selected to prevent gold leaching and enhance the catalytic activity of supported AuNPs [79].

The reduction of NB was thus first studied under different temperature, catalyst loading, and reaction time conditions, and the results are summarised in Table 1.

Table 1. Reduction of NB catalysed by AuNPs-PPO under different experimental conditions.



Entry ^a	T (°C)	NB/Au (Molar Ratio)	Time (min)	Conversion ^b (%)	Yield ^c (%)	Selectivity ^b (%)			TOF ^d (h ⁻¹)
						AOB	AB	AN	
1	25	250	60	>99	93	-	-	>99	250
2	25	510	60	88	79	7	6	87	452
3	40	510	60	99	94	14	7	79	506
4	60	510	60	>99	91	-	-	>99	510
5	60	1020	60	69	58	58	28	14	701
6	80	1020	60	72	63	60	28	12	734
7	60	1020	120	>99	90	17	9	74	510
8 ^e	60	510	60	92	87	7	4	89	469
9 ^f	60	510	60	98	91	11	6	83	500
10 ^g	60	510	60	99	91	18	9	69	505
11 ^h	60	510	60	72	70	13	7	78	367

^a Reaction conditions: NB (2.55 mmol, 0.42 M), AuNPs-PPO as catalyst, NaBH₄/NB molar ratio = 6, CH₃OH (6 mL), N₂ protective atmosphere (atmospheric pressure). ^b Conversion and selectivity evaluated by ¹H NMR analysis (CD₃OD, 400 MHz, rt). ^c mol_{Products} · mol_{NB}⁻¹ · 100. ^d mol_{converted NB} · mol_{Au}⁻¹ · h⁻¹. ^e CH₃CH₂OH (6 mL) as solvent. ^f H₂O (6 mL) as solvent. ^g NaBH₄/NB molar ratio = 3. ^h NaBH₄/NB molar ratio = 2.

The reported TOF values in the tables correspond to average TOFs, calculated from TON divided by the reaction time, to allow comparison with previously reported catalytic systems in the literature. At room temperature and with a NB/Au molar ratio of 250, NB was completely and selectively converted into AN within 1 h, corresponding to a TOF value of 250 h⁻¹ (Entry 1, Table 1). When the catalyst loading was decreased, corresponding to a higher NB/Au molar ratio of 510, the TOF increased to 452 h⁻¹, although the conversion decreased to 88% and minor amounts of reaction intermediates were detected (Entry 2, Table 1). This result suggests that, under lower catalyst loading, the reduction cascade is not fully completed within the same reaction time, leading to partial accumulation of AOB and AB intermediates.

Increasing the reaction temperature to 40 °C at a NB/Au ratio of 510 afforded almost quantitative nitrobenzene conversion, but the selectivity towards aniline remained moderate due to the persistence of intermediate species (Entry 3, Table 1). A further temperature increases to 60 °C resulted in both quantitative conversion and complete selectivity towards AN after 1 h, with a TOF of 510 h⁻¹ (Entry 4, Table 1). These conditions therefore represent the best compromise between activity and selectivity. At higher substrate-to-metal ratios, the reaction became more sensitive to the balance between conversion and selectivity. For example, after 1 h under the same temperature, the TOF increased to 701 h⁻¹, but the conversion remained incomplete, and the selectivity towards AN was lower (Entry 5, Table 1). A further increase in the temperature to 80 °C slightly improved the conversion, passing from 69% to 72%, while the product distribution remained substantially unchanged (Entry

6, Table 1), indicating that the catalytic efficiency is not simply controlled by temperature but also by the relative rates of the sequential reduction steps.

At NB/Au = 1020 and 60 °C, extending the reaction time to 2 h led to complete conversion, and also the selectivity toward AN also improved (selectivity of 74%), with AOB and AB still present as by-products (Entry 7, Table 1).

Overall, these results indicate that AuNPs-PPO efficiently promotes the NaBH₄-mediated reduction of NB, but the final product distribution strongly depends on the substrate-to-gold ratio, reaction temperature, and reaction time. In particular, complete selectivity towards AN requires conditions that allow not only the initial reduction of the nitro group but also the subsequent conversion of partially reduced intermediates into the final amine.

CH₃OH proved to be the most effective solvent for the selective formation of AN. Under otherwise identical conditions, AuNPs-PPO also remained active in H₂O (Entry 8, Table 1) and CH₃CH₂OH (Entry 9, Table 1), affording high NB conversions of 98% and 92%, respectively. However, the selectivity towards AN decreased in both solvents (Figure 2). This behaviour may be attributed to differences in NaBH₄ stability, substrate solubility, and diffusion of the reacting species within the hydrophobic PPO environment. In particular, CH₃OH likely provides a more favourable balance between substrate solubilisation, reducing-agent activation, and accessibility of NB and reducing agent to the AuNP surface embedded in the polymer matrix.

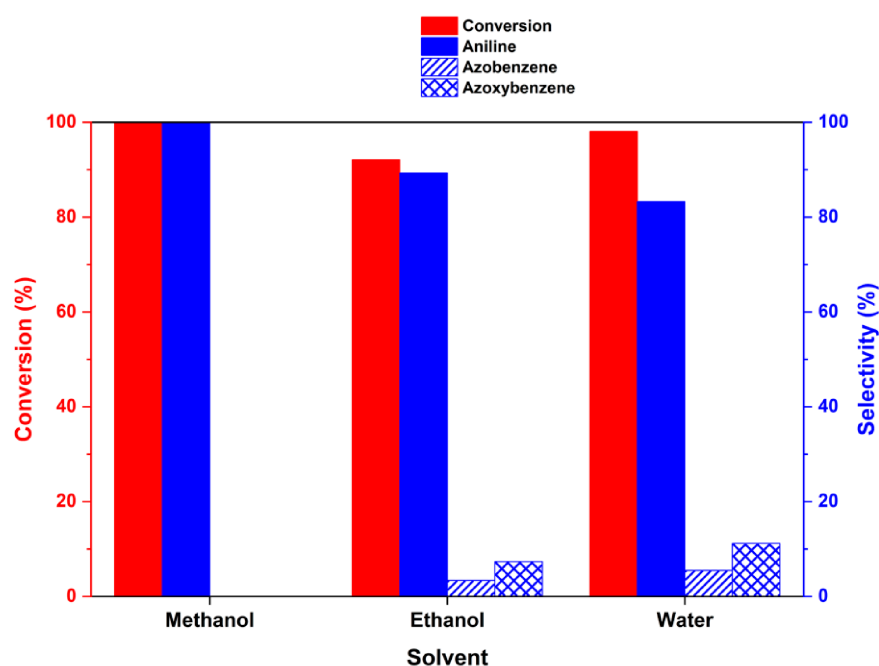


Figure 2. Selectivity of the NB reduction catalysed by AuNPs-PPO in CH₃OH, CH₃CH₂OH and H₂O. [Reaction conditions: NB (2.55 mmol, 0.42 M), AuNPs-PPO (50 mg; 5×10^{-3} mmol_{Au}), NaBH₄/NB molar ratio = 6, T = 60 °C, solvent (6 mL), N₂ protective atmosphere (1 bar), reaction time of 60 min].

The influence of the NaBH₄/NB molar ratio was also examined under the optimised conditions of Entry 4 in Table 1. At a NaBH₄/NB molar ratio of 6, complete and selective conversion of NB into AN was achieved within 60 min. When the NaBH₄/NB molar ratio was decreased to 3 (Entry 10, Table 1), the overall conversion remained essentially unchanged, but the selectivity towards AN slightly decreased, indicating that the reducing equivalents available under these conditions were not sufficient to drive the reaction cascade completely to the final amine. This interpretation is supported by the detection of HB as an intermediate. A further decrease in the NaBH₄/NB molar ratio to 2 (Entry

11, Table 1) resulted in lower conversion and reduced aniline selectivity (Figure 3). These results confirm that a small excess of NaBH_4 is required to ensure full reduction of the nitro functionality and to suppress the accumulation of partially reduced intermediates.

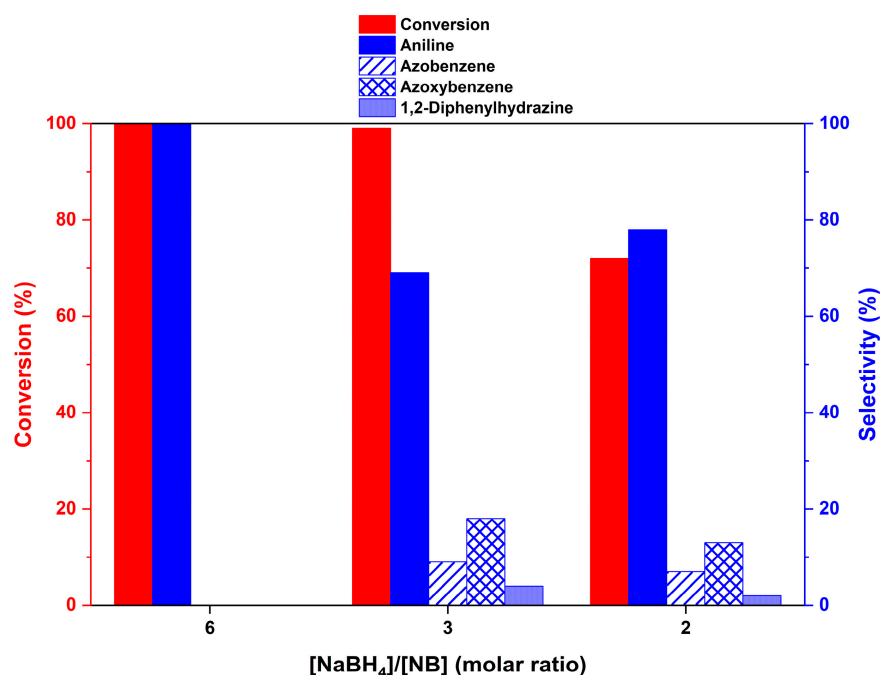


Figure 3. Selectivity of the NB reduction catalysed by AuNPs-PPO with different NaBH_4/NB molar ratios [Reaction conditions: NB (2.50 mmol, 0.42 M), AuNPs-PPO (50 mg; 5×10^{-3} mmol_{Au}), T = 60 °C, CH_3OH (6 mL), N_2 protective atmosphere (1 bar), reaction time of 60 min].

To gain further insight into the catalytic performance of the AuNPs-PPO system, the reduction of NB was monitored over time. As shown in Figure S26a, NB conversion increased steadily, reaching approximately 93% after 60 min. The initial reaction rate, determined from the linear region of the conversion-time profile, was $2.39 \pm 0.05 \text{ \%} \cdot \text{min}^{-1}$, confirming the high activity of the catalyst. The product distribution revealed the formation of AOB and AB as transient intermediates, whose concentrations progressively decreased with reaction time, while AN became the dominant product and was obtained with nearly complete selectivity after 60 min (see Figure S26b). These results are consistent with the well-established consecutive reduction pathway of NB to AN through azoxy- and azo-intermediates.

The recyclability of AuNPs-PPO was investigated over four consecutive catalytic runs under the conditions reported in Entry 1 of Table 1 (see Figure S7). As shown in Figure 4a, both nitrobenzene conversion and AN selectivity remained essentially unchanged throughout the reuse tests, demonstrating the good operational stability of the catalyst. The recycled material was further analysed by ICP-OES and WAXD. ICP-OES analysis after four catalytic runs confirmed that no significant gold leaching occurred during catalysis. In addition, comparison of the WAXD patterns of the fresh and recycled catalysts showed no appreciable variation in the diffraction profile or crystallite size of the AuNPs (Figure 4b), indicating that the nanoparticles do not undergo significant sintering or structural reorganisation under the reaction conditions.

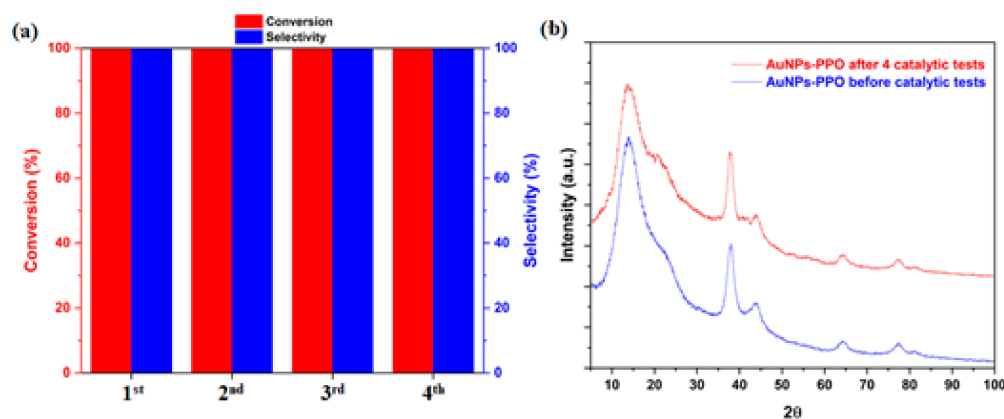


Figure 4. Repeated recycle tests of AuNPs-PPO in NB reduction (graph (a): reaction conditions: NB (6.34 mmol, 0.42 M), AuNPs-PPO (250 mg; 2.50×10^{-2} mmol_{Au}), NaBH₄/NB molar ratio = 6, CH₃OH (15 mL), N₂ protective atmosphere (1 bar), reaction time of 60 min, T = 25 °C); graph (b): WAXD patterns of AuNPs-PPO before and after four catalytic tests..

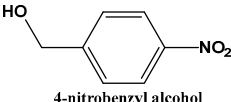
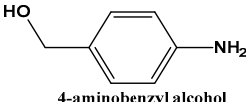
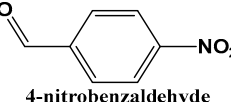
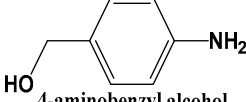
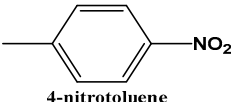
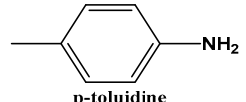
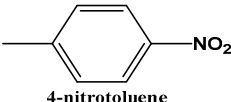
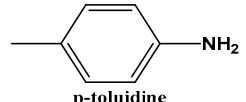
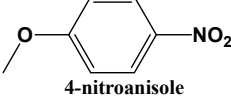
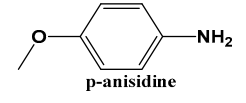
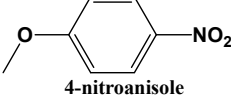
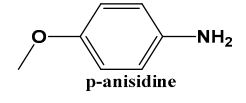
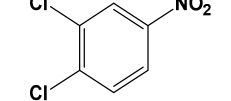
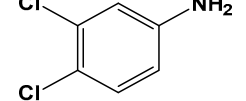
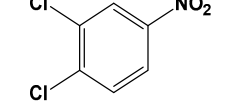
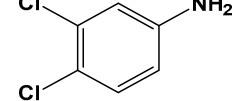
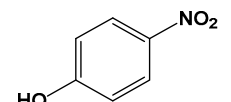
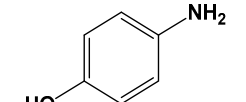
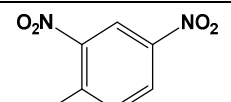
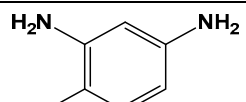
These findings highlight the stabilising role of the PPO matrix, which effectively confines the AuNPs, limits metal leaching, and preserves the structural and electronic features of the active phase during repeated use.

To further assess the substrate scope of the AuNPs-PPO catalytic system, the reduction of a series of para-substituted nitroarenes (p-SNAs) was investigated under NaBH₄-mediated conditions. The results are summarised in Table 2. The catalyst proved effective towards different functionalised nitroarenes, providing the corresponding ANs with high efficiency. In particular, substrates bearing benzylic alcohol and aldehyde functionalities were smoothly converted at room temperature. Complete conversion of 4-nitrobenzyl alcohol was achieved within 1.5 h, whereas 4-nitrobenzaldehyde required 2 h to reach full conversion, corresponding to TOF values of 255 and 127 h^{−1}, respectively. These results indicate that AuNPs-PPO promotes the selective reduction of the nitro group under mild conditions while tolerating additional functional groups that may potentially interact with the catalytic surface as well as with the reducing agent adopted.

For the other p-SNAs, the reduction proceeded more slowly at 35 °C, requiring 6 h to reach quantitative conversion. Under these conditions, TOF values were in the range of 42–45 h^{−1}, indicating that the electronic and/or steric nature of the substituent significantly affects the overall rate of the reduction process. However, when the temperature was increased to 60 °C, complete conversion was generally achieved within only 1 h, with TOF values close to 255 h^{−1}. This marked improvement highlights the strong temperature dependence of the reaction and suggests that the rate-limiting steps of the reduction cascade, including adsorption of the NAs, hydride transfer, and conversion of partially reduced intermediates, are efficiently promoted at a higher temperature of 60 °C, a temperature that can be considered quite sustainable in this field of catalysis.

Overall, the data reported in Table 2 demonstrate that AuNPs-PPO displays a broad catalytic applicability towards SNAs. Most substrates were quantitatively converted into the corresponding ANs under relatively mild conditions, confirming the robustness of the catalyst and the beneficial role of the PPO matrix in stabilising accessible AuNPs. The polymeric environment likely contributes not only to nanoparticle stabilisation but also to the creation of a hydrophobic microenvironment that favours the interaction between aromatic substrates and the catalytically active Au surface.

Table 2. Reduction of SNAs catalysed by AuNPs-PPO.

Entry ^a	T (°C)	Substrate	Time (h)	Conversion ^b (%)	Yield ^c (%)	Product	TOF ^d (h ⁻¹)
1	25	 4-nitrobenzyl alcohol	1.5	>99	89	 4-aminobenzyl alcohol	255
2	25	 4-nitrobenzaldehyde	2	>99	91	 4-aminobenzyl alcohol	127
3	35	 4-nitrotoluene	6	>99	87	 p-toluidine	45
4	60	 4-nitrotoluene	1	>99	89	 p-toluidine	255
5	35	 4-nitroanisole	6	>99	92	 p-anisidine	42
6	60	 4-nitroanisole	1	>99	88	 p-anisidine	255
7	35	 4-nitroaniline	6	>99	93	 1,4-diaminobenzene	42
8	60	 4-nitroaniline	1	>99	91	 1,4-diaminobenzene	253
9	35	 1,2-dichloro-4-nitrobenzene	6	>99	90	 3,4-dichloroaniline	42
10	60	 1,2-dichloro-4-nitrobenzene	1	>99	87	 3,4-dichloroaniline	254
11	60	 4-nitrophenol	1	60	54	 4-aminophenol	153
12 ^e	60	 2,4-dinitrophenol	1	>99	n.d.	 2,4-diaminophenol	254

^a Reaction conditions: SNAs (2.53–2.55 mmol), AuNPs-PPO (100 mg; 10×10^{-3} mmol_{Au}), NaBH₄/s-NB molar ratio = 6, CH₃OH (6 mL), N₂ protective atmosphere (1 bar). ^b Conversion and selectivity evaluated by ¹H NMR analysis (CD₃OD, 400 MHz, rt). ^c mol_{Products} · mol_{SNAs}⁻¹ · 100. ^d mol_{convertedSNAs} · mol_{Au}⁻¹ · h⁻¹. ^e NaBH₄/SNAs molar ratio = 12 and (E)-4,4'-(diazene-1,2-diyl)bis(2-aminophenol) as byproduct (30%).

A different behaviour was observed for the substrate reported in Entry 11. Under the standard conditions used for the other substrates, namely 60 °C, 1 h, and a NaBH₄/substrate molar ratio of 6, only 60% conversion was obtained, although the corresponding TOF remained appreciable at 153 h⁻¹. This result suggests that this substrate is more difficult to reduce, probably because of a less favourable adsorption geometry, electronic deactivation, or competitive stabilisation of partially reduced intermediates. Increasing the NaBH₄/substrate molar ratio to 12 restored quantitative conversion within 1 h, with a TOF of 254 h⁻¹. However, this improvement in conversion was accompanied by the formation of a small amount of (E)-4,4'-(diazene-1,2-diyl)bis(2-aminophenol), detected as a by-product in 30% yield. This finding indicates that, for this specific substrate, an increased amount of reducing agent favours the overall consumption of the NA but does not fully suppress competitive coupling pathways involving partially reduced intermediates. The formation

of the azo derivative is consistent with the well-known stepwise reduction pathway of nitroarenes, in which nitroso, hydroxylamine, azoxy, azo, and hydrazo intermediates may be involved before complete conversion to the corresponding aniline.

Taken together, these results confirm that AuNPs-PPO is an efficient and versatile catalyst for the NaBH_4 -mediated reduction of SNAs. The system combines high conversion, good functional-group tolerance, and short reaction times under optimised conditions. The comparison between the reactions performed at 35 and 60 °C further demonstrates that temperature plays a key role in driving the complete reduction of the nitro group, especially for less reactive substrates. At the same time, the behaviour observed for Entry 11 highlights that substrate structure can influence not only the reaction rate but also the selectivity of the reduction pathway. Therefore, while AuNPs-PPO provides a robust catalytic platform for nitroarene reduction, fine-tuning of the NaBH_4 /substrate ratio may be required for substrates prone to azo-type side reactions.

3. Discussion

Table 3 compares the catalytic performance of AuNPs-PPO with selected AuNP-based systems previously reported for the NaBH_4 -mediated reduction of NAs. Overall, the data show that AuNPs-PPO reaches quantitative or near-quantitative conversion for several SNAs under mild conditions, generally using low Au loading, short reaction times, and CH_3OH as solvent. In the model reduction of nitrobenzene, AuNPs-PPO affords quantitative conversion within 1 h, with TOF values up to 510 h^{-1} under optimised conditions. This activity is lower than the exceptionally high TOFs reported for some highly engineered systems, such as AuNPs@PAF-184/185 or resin-trapped AuNPs, but it compares favourably with several other AuNP catalysts operating under comparable or even more demanding conditions, including AuNPs-MTA, AuNPs-GO, AuNPs-P(STY@NIPM), AuNPs-Starch-crt, and AuNPs-Mg-AP (Table 3). A key advantage of AuNPs-PPO is not merely the absolute TOF value, but the balance between activity, selectivity, catalyst accessibility, and simplicity of preparation. PPO is a commercially available, inexpensive, and thermally stable polymer, and the catalyst can be obtained through a straightforward procedure leading to small and well-dispersed Au nanoparticles embedded in the polymer matrix. This contrasts with several high-performing catalysts that require more complex supports, such as functionalized magnetic polymer brushes, porous aromatic frameworks, polysaccharide composites, or resin-based systems. For example, PAF-supported AuNPs show outstanding apparent activities, with NB reduction occurring within seconds; however, these materials rely on specifically designed cationic porous aromatic frameworks, high Au loading, and multi-step synthesis. In this context, AuNPs-PPO represents a more practical and readily accessible catalytic platform.

The comparison with the AuNPs-sPSB catalyst, which previously reported, is particularly informative [42]. That system displayed very high activity, especially for NB and 4-nitrobenzaldehyde, and demonstrated the crucial role of the nanoporous polymer phase in controlling both activity and selectivity. In that study, non-permeable crystalline forms favoured partial reduction and accumulation of azoxy/azo intermediates, whereas porous δ/ϵ forms of syndiotactic polystyrene promoted complete reduction to AN through a condensation-type pathway. The present AuNPs-PPO system follows the same conceptual line: a hydrophobic and nanoporous polymeric environment stabilises accessible AuNPs and modulates substrate diffusion, adsorption, and interaction with the active metal surface. However, compared with sPSB, PPO offers a simpler and commercially more accessible polymeric matrix, while preserving high catalytic performance and selectivity.

The substrate scope further supports the versatility of AuNPs-PPO. Electron-rich nitroarenes such as 4-nitrotoluene and 4-nitroanisole, as well as functionalized substrates

such as 4-nitrobenzaldehyde and 4-nitroaniline, are efficiently converted under optimised conditions. The lower conversion observed for 4-nitrophenol under standard conditions highlights that substrate structure and acid/base properties can strongly affect the reaction outcome, probably by modifying adsorption, nitrophenolate formation, and the stability of partially reduced intermediates. This point is relevant because it shows that AuNPs-PPO is not simply an activity-driven catalyst, but a system whose selectivity can be tuned by solvent, temperature, and NaBH_4 /substrate ratio. Overall, compared with previously reported catalysts, AuNPs-PPO emerges as a robust, selective, reusable, and synthetically simple alternative to more elaborate polymer-supported AuNP catalysts.

The reduction of nitroarenes by NaBH_4 over supported AuNPs is generally interpreted as a surface-mediated hydrogen-transfer process. NaBH_4 is activated at the Au surface, generating Au–H-like species or related surface hydride equivalents able to reduce the adsorbed nitroarene. Previous mechanistic studies on AuNP-based systems have shown that B–H bond activation can be involved in the rate-determining step and that electron-withdrawing substituents usually accelerate the reaction, in agreement with a hydride/electron-transfer pathway toward the nitro group. In the classical Haber-type description, NB reduction may proceed either through a direct route involving nitroso and hydroxylamine intermediates, or through a condensation route in which nitroso and hydroxylamine species couple to form AOB, AB, and HB before final conversion to AN. The product distribution observed in the AuNPs-PPO-catalysed reduction of NAs is consistent with this mechanistic framework. Under optimised conditions, NB and several SNAs are selectively converted into the corresponding ANs with excellent yields. Conversely, under less favourable conditions, especially at lower NaBH_4 /substrate ratios, partially reduced products such as AOB, AB, and HB are detected. This indicates that the reaction does not proceed through a single elementary step, but rather through a sequence of surface-mediated reduction and condensation events, in which the relative rates of intermediate hydrogenation, desorption, and coupling determine the final selectivity. In this context, the PPO matrix should not be regarded as a passive stabilizing support, but as an active polymeric microenvironment that contributes to the catalytic behaviour. Its hydrophobic and nanoporous nature may favour the diffusion and local concentration of NAs near the AuNP surface, while also affecting the residence time and further reduction of reactive intermediates. This interpretation is further supported by related reports on AuNPs confined in porous organic polymers, where *N*-phenylhydroxylamine (PHA), AOB, and HB were identified as intermediates on the way to AN. Thus, the formation of azo-type products under non-optimized conditions suggests that partially reduced nitrogen-containing intermediates can accumulate and undergo condensation when hydride availability or mass transfer becomes less favourable. A further useful comparison can be made with the work of Su et al., who investigated AuNPs confined within imidazolium-based porous organic polymers for NA reduction [80]. This study is particularly relevant because it combines a porous organic support with AuNP-catalysed NaBH_4 activation, thus providing a mechanistic parallel to the present AuNPs-PPO system. Su et al. observed that the reduction of nitrobenzene may involve PHA, AOB, and HB as reaction intermediates, supporting a stepwise pathway in which direct hydrogenation competes with condensation reactions between partially reduced nitrogen-containing species. The detection of analogous azo-type intermediates in the present study under non-optimized conditions, therefore, reinforces the idea that AuNPs-PPO follows a related mechanistic scenario. However, while imidazolium-based porous organic polymers require the synthesis of specifically designed ionic frameworks, PPO provides a commercially available and synthetically simpler hydrophobic polymer matrix. In this sense, AuNPs-PPO retains the mechanistic

advantages associated with porous organic confinement, while offering a more accessible catalytic platform.

Overall, the mechanistic picture emerging from this study is that AuNPs-PPO promotes NA reduction through the cooperative action of Au-mediated NaBH_4 activation and polymer-controlled confinement effects. The AuNPs are responsible for hydride activation and hydrogen transfer, whereas the PPO matrix stabilises small AuNPs, controls substrate access, and influences the fate of reactive intermediates. This dual role explains the high selectivity toward anilines under optimised conditions, and the formation of diagnostic azo-type intermediates under less reducing conditions. Compared with the previously reported AuNPs-sPSB catalyst, AuNPs-PPO preserves the beneficial features of a nanoporous polymer-supported Au system while relying on a commercially available, thermally stable, and synthetically simpler polymer matrix.

Table 3. Comparison between AuNPs-PPO catalyst and previously reported catalysts for the reduction of NAs using NaBH_4 as reducing agent.

Catalyst	Au Loading (mol%)	Solvent	T (°C)	Time (h)	Substrate	Conv. (%)	TON ^a	TOF ^a (h ^{−1})	Ref.
AuNPs-PPO	0.1	CH ₃ OH	25	1	NB	>99	250	250	This work
AuNPs-PPO	0.2	CH ₃ OH	60	1	NB	>99	510	510	This work
AuNPs-PPO	0.1	CH ₃ OH	60	1	4-nitrotoluene	>99	255	255	This work
AuNPs-PPO	0.1	CH ₃ OH	60	1	4-nitroanisole	>99	255	255	This work
AuNPs-PPO	0.1	CH ₃ OH	25	2	4-nitrobenzaldehyde	95	254	127	This work
AuNPs-PPO	0.1	CH ₃ OH	60	1	4-nitroaniline	>99	253	253	This work
AuNPs-PPO	0.1	CH ₃ OH	60	1	4-nitrophenol	60	153	153	This work
AuNPs-sPSB (Cε)	0.2	CH ₃ OH	35	0.75	NB	>99	500	667	[42]
AuNPs-sPSB (Cε)	0.1	CH ₃ OH	25	2	4-nitrobenzaldehyde	>99	1000	500	[42]
AuNPs-sPSB (Cε)	0.1	CH ₃ OH	35	6	4-nitroanisole	>99	1000	167	[42]
MNP@PGMA@DAP@AuNPs	0.5	H ₂ O	25	0.08	4-nitroaniline	97	194	2425	[46]
AuNPs-MTA	1	EtOH	25	1	4-nitrobenzaldehyde	98	98	98	[81]
AuNPs-MTA	1	EtOH	25	3	NB	95	96	32	[81]
AuNPs-Starch-crt	0.1	H ₂ O	25	4	4-nitrotoluene	89	888	222	[82]
AuNPs-GO	0.3	H ₂ O	25	35	NB	92	315	9	[83]
AuNPs-GO	0.3	H ₂ O	25	45	4-nitroaniline	93	315	7	[83]
AuNPs/TiO ₂	0.1	EtOH	25	0.33	4-nitroaniline	95	130	394	[84]
AuNPs-P(STY@NIPM)	1	H ₂ O	28	0.13	4-nitroaniline	>99	8	63	[49]
AuNPs-Mg-AP	0.005	H ₂ O	25	1	NB	98	211	211	[85]
AuNPs-Mg-AP	0.005	H ₂ O	25	1	4-nitrotoluene	>99	213	213	[85]
resin-AuNPs/AuNPs–Amberlite XAD-4	0.06	CH ₃ OH/H ₂ O	40	0.33	NB	85	1328	4024	[86]
resin-AuNPs/AuNPs–Amberlite XAD-4	0.06	CH ₃ OH/H ₂ O	40	0.42	4-nitroaniline	95	1484	3534	[86]
resin-AuNPs/AuNPs–Amberlite XAD-4	0.06	CH ₃ OH/H ₂ O	40	0.42	4-nitrobenzaldehyde	85	1328	3162	[86]
AuNPs-CS-XG	0.05	H ₂ O	50	2	NB	95	1900	950	[50]
AuNPs-CS-XG	0.05	H ₂ O	50	2	4-nitroanisole	95	1900	950	[50]
AuNPs-CS-XG	0.05	H ₂ O	50	2	4-nitrotoluene	95	1900	950	[50]
AuNPs-CS-XG	0.05	H ₂ O	50	3	4-nitroaniline	95	1899	633	[50]
AuNPs@PAF-184	0.5	H ₂ O	25	0.003	NB	96	192	64,000	[48]
AuNPs@PAF-184	0.5	H ₂ O	25	0.003	4-nitrotoluene	96	192	64,000	[48]
AuNPs@PAF-185	0.5	H ₂ O	25	0.003	NB	95	190	63,333	[48]
AuNPs@PAF-185	0.5	H ₂ O	25	0.003	4-nitrotoluene	95	190	63,333	[48]
AuNPs/Al ₂ O ₃	0.34	H ₂ O	25	0.017	4-nitrophenol	82	248	14,600	[87]
AuNPs-MPS	25.8	H ₂ O	25	2	4-nitrophenol	90	4	2	[88]
AuNPs-CeO ₂	0.2	H ₂ O	25	0.5	4-nitrophenol	90	450	900	[47]

^a TON and TOF values are reported as given in the original references or calculated from available data. They should be regarded as approximate comparative parameters, since reaction conditions, substrate, catalyst loading, conversion level, and calculation methods may differ among the reported studies.

4. Experimental Section

4.1. Materials

$\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (49 wt% Au; Merck, Darmstad, Germany), poly(2,6-dimethyl-1,4-phenylene oxide) (PPO; Sigma-Aldrich, Darmstad, Germany), sodium borohydride (NaBH_4 , 98%, Sigma-Aldrich) sodium triethylborohydride (NaBHET_3 , 1.0 M in toluene; Sigma-Aldrich), methanol (CH_3OH ; $\geq 99.8\%$; Sigma-Aldrich), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$; $\geq 99.8\%$; Sigma-Aldrich), water (H_2O , High-Performance Liquid Chromatography (HPLC) grade; Pancreac, Darmstad, Germany), toluene (anhydrous, 99.8%; Sigma-Aldrich), n-

hexane ($\geq 95\%$; Sigma-Aldrich), 4-nitrobenzyl alcohol (99%; Sigma-Aldrich), nitrobenzene (NB, $>99.5\%$; Fluka, Darmstadt, Germany), 4-nitrobenzaldehyde (98%; Sigma-Aldrich), 4-nitroaniline ($\geq 99.8\%$; Sigma-Aldrich), 4-nitrotoluene (99%; Sigma-Aldrich), 4-nitroanisole (97%; Sigma-Aldrich), 1,2-dichloro-4-nitrobenzene (99%; Sigma-Aldrich), tetrahydrofuran (THF, 99%, Sigma-Aldrich) purified with lithium aluminium hydride (LiAlH_4 , 95%, Sigma-Aldrich). For ICP analysis: nitric acid (HNO_3 , 65%, Sigma-Aldrich), sulfuric acid (H_2SO_4 , 98%, Sigma-Aldrich), hydrogen peroxide (H_2O_2 , 30%w/w in H_2O , Sigma-Aldrich).

4.2. Instrumentation and Methods

The Nuclear Magnetic Resonance (NMR) spectra were recorded at 25 °C using Bruker Avance 400 or Bruker Avance 600 spectrometers (Karlsruhe, Germany), unless otherwise stated. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. (Tewksbury, MA, USA), degassed and dried over activated 4Å molecular sieves prior to use. Chemical shifts (δ) are listed as parts per million and coupling constants (J) in hertz (Hz) and referred to tetramethylsilane as an external reference, using residual proton signals of deuterated solvent. ^1H NMR spectra are referenced using the residual solvent peak at δ 3.31 for CD_3OD . The NMR characterisation of the reaction products was performed using the following ^1H and ^{13}C NMR diagnostic signals in CD_3OD at room temperature: aniline [(400 MHz): 7.01 (m, 2H), 6.66 (d, 2H, $J = 7.9$ Hz), 6.60 (m, 1H), 5.10 (br s, 2H)]; (100 MHz): 148.47, 129.91, 119.18, 116.56 (see Figure S10); azobenzene [(600 MHz): 8.08 (d, 4H, $J = 8.2$ Hz), 7.49 (m, 4H), 7.35 (m, 2H)]; azoxybenzene [(600 MHz): 8.22 (d, 2H, $J = 7.7$ Hz), 7.54 (m, 1H), 7.43 (m, 2H), 7.13 (m, 2H), 6.92 (d, 2H, $J = 8.2$ Hz), 6.78 (m, 1H)] (see Figure S8); p-toluidine [(400 MHz): 6.82 (d, 2H, $J = 7.9$ Hz), 6.58 (d, 2H, $J = 8.1$ Hz), 5.13 (br s, 2H), 2.12 (s, 3H)] (see Figure S6); (100 MHz): 145.58, 130.39, 128.66, 116.94, 20.48 (see Figure S12); p-anisidine [(600 MHz): 6.66 (br s, 4H), 4.95 (br s, 2H), 3.65 (s, 3H)] (see Figure S3); (100 MHz): 154.37, 141.48, 118.14, 115.58, 56.01 (see Figure S13); 1,4-diaminobenzene [(400 MHz): 6.58 (s, 4H), 4.93 (br s, 4H)] (see Figure S4); (100 MHz): 140.12, 118.40 (see Figure S14); 4-aminobenzyl alcohol [(400 MHz): 7.05 (d, 2H, $J = 7.7$ Hz), 6.66 (d, 2H, $J = 7.7$ Hz), 4.98 (br s, 2H), 4.41 (s, 2H)] (see Figure S2); (100 MHz): 147.95, 132.06, 129.43, 116.36, 65.24 (see Figure S15); 3,4-dichloroaniline [(600 MHz): 7.07 (d, 1H, $J = 8.6$ Hz), 6.75 (d, 1H, $J = 2.64$ Hz), 6.52 (dd, 1H, $J_1 = 8.63$ Hz, $J_2 = 2.61$ Hz)] (see Figure S5); (100 MHz): 149.37, 133.23, 131.48, 120.34, 116.98, 115.70 (see Figure S11); p-aminophenol [(400 MHz): 6.58 (m, 4H)] (see Figure S9); 2,4-diaminophenol [(400 MHz): 6.52 (d, 1H, $J = 8.29$ Hz), 6.30 (s, 1H), 6.09 (dd, 1H, $J_2 = 8.25$ Hz, $J_1 = 2.71$ Hz)].

The surface area of the polymer matrix was determined by nitrogen adsorption measurements at 77 K on AuNPs-PPO powder, which was degassed under vacuum at 40 °C for 24 h prior to analysis. Measurements were performed using a Nova Quantachrome 4200e instrument, and the specific surface area was calculated according to the Brunauer-Emmett-Teller (BET) method. Wide-angle X-ray diffraction (WAXD) patterns were recorded in reflection mode using a Bruker D8 automatic powder diffractometer equipped with nickel-filtered $\text{CuK}\alpha$ radiation [89]. The gold content in the AuNPs-PPO catalyst was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) using a Thermo Fisher Scientific iCAP 6000 instrument. For analysis, 50 mg of the catalyst was digested in a Kjeldahl flask with 2.5 mL of concentrated H_2SO_4 (98 wt%) at 250 °C for 30 min. After cooling to room temperature, 4.0 mL of H_2O_2 (30 wt%) was added, and the mixture was reheated at 250 °C until a clear solution was obtained. Subsequently, 1.5 mL of freshly prepared aqua regia was added at room temperature, and the solution was diluted to a final volume of 10.0 mL with 10 vol% aqueous HCl. Calibration was performed using four gold(III) standard solutions of varying concentrations, obtained by serial dilution of a certified standard solution (1.000 ± 0.002 g/L in water with 2 wt% HCl)

with water and 10 vol% HCl. Electron microscopy analyses were conducted with a Thermo Fisher TALOS F200X G2 microscope. High-resolution transmission electron microscopy (HR-TEM) and scanning transmission electron microscopy–energy-dispersive X-ray spectroscopy (STEM-EDX) mapping were performed using a 200 kV accelerating voltage [90]. Gold d-spacing values were identified by comparison with the cubic Au (entry 1744486) from the Cambridge Crystallographic Data Centre (CCDC). Particle size distribution was estimated by measuring one hundred particles from TEM and STEM images collected from various regions of the sample. In the case of elongated particles, the longest diagonal was used for size estimation. X-ray electron spectroscopy (XPS) measurements were carried out using a non-monochromated Mg-K α X-ray source (1253.6 eV) and a VSW HAC 5000 hemispherical electron energy analyser.

4.3. Synthesis of AuNPs-PPO

AuNPs-PPO was prepared according to a previously reported procedure to obtain a gold catalyst containing 2 wt% of gold. Finely ground PPO (4.90 g) was suspended in anhydrous THF (800 mL) in a 1 L three-neck round-bottom flask equipped with a magnetic stirrer, and the mixture was stirred under nitrogen at room temperature for 24 h [59,91]. The suspension was then heated to reflux for 1 h to ensure complete polymer swelling. After cooling to room temperature, H₂AuCl₄·3H₂O (0.200 g, 5.08×10^{-4} mol) was added and stirred for 1 h. A solution of NaBH₄ (4.1 mL, 1 M in toluene) was then added, resulting in an immediate colour change from pale yellow to red. The resulting catalyst was quickly precipitated in CH₃OH, collected by filtration, washed with fresh CH₃OH (3 × 200 mL), and dried under vacuum at room temperature for 16 h.

4.4. General Procedure for Reduction of NAs Catalysed by AuNPs-PPO (Referred to Entry 1 of Table 1)

A 25 mL round-bottomed flask equipped with a magnetic stirrer bar was charged with NB (0.308 g; 2.50×10^{-3} mol), AuNPs-PPO (100 mg; 1×10^{-5} mol_{Au}), CH₃OH (6 mL) and stirred for 10 min at 25 °C. After that, NaBH₄ (0.580 g; 15.3×10^{-3} mol) was quickly added; the system was quickly equipped with a condenser and a nitrogen atmosphere was used. The mixture was stirred for 1 h at 25 °C. The flask was cooled to room temperature, centrifuged for 15 min, and the supernatant phase was analysed by ¹H NMR spectroscopy using methanol-*d*₄ (CD₃OD) as a solvent, determining a conversion of >99%. The supernatant phase was processed to determine the isolated yield of the reaction. CH₃OH was removed under reduced pressure using a rotary evaporator at 25 °C. H₂O (3 mL) and toluene (5 mL) were then added, and the mixture was transferred to a separatory funnel. The organic phase was separated, while residual inorganic species derived from NaBH₄ were removed through the aqueous phase. The organic layer was dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure at 80 °C using a rotary evaporator. Residual toluene was removed by co-evaporation with n-hexane under reduced pressure at 60 °C. The resulting product was finally dried under vacuum at 60 °C overnight prior to weighing and isolated yield determination. The mass balance, based on the quantitative ¹H NMR analysis of the detected organic species, was calculated as the sum of the moles of all reaction products divided by the initial moles of NB, multiplied by 100.

4.5. General Procedure for Catalyst Recycling Tests

A 25 mL round-bottomed flask equipped with a magnetic stirrer bar was charged with NB (0.870 g; 6.34×10^{-3} mol), AuNPs-PPO (250 mg; 2.5×10^{-5} mol_{Au}), CH₃OH (15 mL) and NaBH₄ (1.44 g; 0.038 mol). Then, the system was equipped with a condenser and a nitrogen atmosphere was used. The mixture was stirred for 1 h at 25 °C. The flask

was cooled to room temperature, centrifuged, and the supernatant phase analysed by ^1H NMR spectroscopy using CD_3OD as a solvent to determine the conversion. The catalyst was recovered by filtration, washed with fresh CH_3OH , and dried under vacuum at room temperature for 16 h. The same procedure was repeated for other catalytic tests.

5. Conclusions

In this work, AuNPs supported within a PPO matrix were investigated as heterogeneous catalysts for the NaBH_4 -mediated reduction of NAs to the corresponding ANs. The adopted synthetic procedure enabled the controlled incorporation of AuNPs into the PPO support, affording small and well-dispersed metallic nanoparticles with an average size of approximately 4–5 nm, as confirmed by WAXD and electron microscopy analyses. The PPO matrix proved effective in stabilising the AuNPs, limiting aggregation and preserving the accessibility of the active metal surface.

AuNPs-PPO showed high catalytic activity in the reduction of NB under mild conditions, reaching quantitative conversion and complete selectivity to AN within 1 h. TOF values up to 734 h^{-1} were observed at higher substrate/Au ratios, although quantitative and selective AN formation was achieved with a TOF of 510 h^{-1} . The reaction outcome was strongly affected by the experimental parameters, particularly temperature, solvent, catalyst loading, and NaBH_4 /substrate ratio. CH_3OH was identified as the most suitable solvent, providing the best balance between substrate solubilisation, NaBH_4 activation, and access of the reacting species to the AuNP surface confined within the hydrophobic polymer matrix.

The formation of partially reduced intermediates such as AOB, AB, and HB provided useful mechanistic information. These observations support a stepwise reduction pathway in which Au-mediated hydride activation cooperates with the polymer-controlled microenvironment. In this framework, the PPO support does not behave simply as an inert stabilising matrix, but contributes to modulating substrate diffusion, intermediate residence time, and final product selectivity.

The catalytic system also displayed broad applicability toward SNAs, including electron-rich and functionalised substrates. Most p-SNAs were efficiently converted into the corresponding ANs under relatively mild conditions, although the behaviour of more demanding substrates, such as nitrophenol derivatives, highlighted the importance of fine-tuning the NaBH_4 /substrate ratio to suppress competitive azo-type coupling pathways. Importantly, AuNPs-PPO maintained high conversion and selectivity over four consecutive catalytic cycles, with no significant gold leaching or nanoparticle sintering, confirming the stabilising role of the PPO matrix.

Overall, AuNPs-PPO emerges as a robust, selective, reusable, and synthetically simple catalyst for NAs reduction. Compared with more elaborate polymer-supported AuNP systems, the present catalyst combines good catalytic performance with the practical advantages of a commercially available, thermally stable, and inexpensive polymer support. These features make AuNPs-PPO a promising platform for sustainable nitroarene reduction protocols relevant to fine chemical synthesis and environmental remediation.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal16080701/s1>. Figure S1: ^1H NMR of aniline (400 MHz, CD_3OD , 25°C , Entry 1-Table 1); Figure S2: ^1H NMR of 4-aminobenzyl alcohol (400 MHz, CD_3OD , 25°C , Entry 2-Table 2); Figure S3: ^1H NMR of p-anisidine (600 MHz, CD_3OD , 25°C , Entry 5-Table 2); Figure S4: ^1H NMR of 1,4-diaminobenzene (400 MHz, CD_3OD , 25°C , Entry 8-Table 2); Figure S5: ^1H NMR of 3,4-dichloroaniline (600 MHz, CD_3OD , 25°C , Entry 10-Table 2); Figure S6: ^1H NMR of p-toluidine (600 MHz, CD_3OD , 25°C , Entry 4-Table 2); Figure S7: ^1H NMR of aniline obtained in repeated recycle tests of AuNPs-PPO in NB reduction (400 MHz, CD_3OD , 25°C). Reaction conditions:

NB (6.34 mmol, 0.42 M), AuNPs-PPO (250 mg; $2.50 \cdot 10^{-2}$ mmol), NaBH_4 /NB molar ratio of 6, solvent (15 mL), $T = 25^\circ\text{C}$, N_2 protective atmosphere (1 bar), reaction time of 60 min); Figure S8: ^1H NMR of reaction mixture (600 MHz, CD_3OD , 25°C , Entry 2-Table 1); Figure S9: ^1H NMR of reaction mixture (600 MHz, CD_3OD , 25°C , Entry 11-Table 1); Figure S10: ^{13}C NMR of aniline (100 MHz, CD_3OD , 25°C , Entry 1-Table 1); Figure S11: ^{13}C NMR of 3,4-dichloroaniline (100 MHz, CD_3OD , 25°C , Entry 10-Table 2); Figure S12: ^{13}C NMR of p-toluidine (100 MHz, CD_3OD , 25°C , Entry 4-Table 2); Figure S13: ^{13}C NMR of p-anisidine (100 MHz, CD_3OD , 25°C , Entry 5-Table 2); Figure S14: ^{13}C NMR of 1,4-diaminobenzene (100 MHz, CD_3OD , 25°C , Entry 8-Table 2); Figure S15: ^{13}C NMR of 4-aminobenzyl alcohol (100 MHz, CD_3OD , 25°C , Entry 2-Table 2); Figure S16: COSY NMR of aniline (600 MHz, CD_3OD , 25°C , Entry 1-Table 1); Figure S17: HSQC NMR of aniline (600 MHz, CD_3OD , 25°C , Entry 1-Table 1); Figure S18: COSY NMR of p-toluidine (600 MHz, CD_3OD , 25°C , Entry 4-Table 2); Figure S19: HSQC NMR of p-toluidine (600 MHz, CD_3OD , 25°C , Entry 4-Table 2); Figure S20: COSY NMR of p-anisidine (600 MHz, CD_3OD , 25°C , Entry 5-Table 2); Figure S21: COSY NMR of 1,4-diaminobenzene (600 MHz, CD_3OD , 25°C , Entry 8-Table 2); Figure S22: HSQC NMR of 1,4-diaminobenzene (600 MHz, CD_3OD , 25°C , Entry 8-Table 2); Figure S23: COSY NMR of 3,4-dichloroaniline (600 MHz, CD_3OD , 25°C , Entry 10-Table 2); Figure S24: HSQC NMR of 3,4-dichloroaniline (600 MHz, CD_3OD , 25°C , Entry 10-Table 2); Figure S25: COSY NMR of reaction mixture with 4-nitro- and 4-aminophenol (600 MHz, CD_3OD , 25°C); Figure S26: Reaction profile for the NB reduction catalyzed by AuNPs-PPO (Entry 1-Table 1); Figure S27: AuNPs-PPO catalyst: (a) Before catalytic run; (b) After 4 four catalytic runs washed with CH_3OH and dried under vacuum at room temperature for 16 h; Figure S28: Sample of kinetic test after centrifugation and filtration; Figure S29. Experimental setup of the reaction: (a) Mixture reaction with AuNPs-PPO catalyst, NB and CH_3OH ; (b) Reaction in N_2 atmosphere; (c) End of the reaction before centrifugation.

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