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Authors: Titel Jurca, Lorianne R. Shultz, Lin Hu, Konstantin Preradovic, Melanie J. Beazley, and Xiaofeng Feng

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A broader-scope analysis of the catalytic reduction of nitrophenols and azo dyes with noble metal nanoparticles

Lorianne R. Shultz,^[a] Lin Hu,^[b] Konstantin Preradovic,^[a] Melanie J. Beazley,^{*[a]} Xiaofeng Feng,^{*[b][c][d]} Titel Jurca^{*[a][d]}

Abstract: In addition to the broad environmental implications associated with the removal of nitroaromatics from industrial effluent, the catalytic reduction of 4-nitrophenol (4NP) has emerged as a benchmark model for quantifying catalytic activity of metal nanoparticles. Here we present a series of noble metal nanoparticles immobilized on amorphous carbon (Au@C, Ag@C, Pt@C and Pd@C). All materials show competitive catalytic activity over 4NP, amino-substituted nitrophenols (ANPs) and azo dyes. Overall, Pd@C exhibits superior activity that increases further when exposed to recycling protocol. Moreover, testing all materials synthesized over a broader substrate scope with added functionalities reveals inconsistencies in the prognosticating ability of the ubiquitous 4NP model reaction. By incorporating variably substituted ANPs into the substrate scope and averaging performance, the resulting rank of catalyst activity more accurately reflects activity trends when applied to other reducible functionalities, such as -N=N- groups in azo dyes.

Para-nitrophenol (4NP), and more broadly nitroaromatic compounds are widely used in industrial processes for the manufacture of pharmaceuticals, pesticides, pigments, dyes, and explosives.^[1] It is thus not surprising that nitroaromatic compounds are one of the most common anthropogenic water pollutants in industrial effluent. Many of these compounds are acutely toxic, mutagenic and either suspected or established carcinogens.^[2] However, within the context of **4NP**, the reduction product is 4-aminophenol (4AP), a significantly less toxic and chemical intermediate the important in synthesis of photographic agrochemicals, dyes, developers, and pharmaceuticals (e.g. paracetamol).^[3] Thus, access to 4AP, and similarly derived amino-phenols via mild, aqueous phase catalytic reduction of 4NP has emerged as an important area of research.[4]

Conversely, due to its reliable simplicity, the reduction of 4nitrophenol (**4NP**) with NaBH₄ under aqueous conditions has become a benchmark model reaction for quantifying the catalytic

[a]	L. R. Shultz, K. Preradovic, Prof. M. J. Beazley, Prof. T. Jurca
	Department of Chemistry, University of Central Florida
	Orlando, Florida, 32816, USA
	E-mail: Titel.Jurca@ucf.edu
[b]	L. Hu, Prof. X. Feng
	Department of Materials Science and Engineering, University of
	Central Florida
	Orlando, Florida, 32816, USA
[c]	Prof. X. Feng,
	Department of Physics, University of Central Florida
	Orlando, Florida, 32816, USA
[d]	Prof. X. Feng, Prof. T. Jurca
	Renewable Energy and Chemical Transformations Cluster,
	University of Central Florida
	Orlando, Florida, 32816, USA
	Supporting information for this article is given via a link at the end of
	the document.

activity of metal nanoparticles.^[5] The majority of this work to date, and the mechanistic understanding derived from it, is based on noble metal nanoparticles (*e.g.* Pd, Pt, Ag, and Au).^[6] However, in the past decade, efforts have expanded to include systems based on other transition metals, and even metal-free systems.^[7]

When conducted in the presence of excess NaBH4, as is common practice, the reduction of 4NP to 4AP (Scheme 1) is typically described in terms of the Langmuir-Hinshelwood model.^[5a,8] Therein, reactants **4NP*** and NaBH₄-derived surface hydrogen species are first adsorbed onto the catalyst surface in a rapid, reversible process. The reaction proceeds in a pseudo-first order manner via a series of intermediates including 4nitrosophenol and 4-hydroxylaminophenol (Scheme S1)^[9] ultimately yielding 4AP*, which rapidly desorbs from the surface, thus having little impact on reaction kinetics (Schemes 1 and S1). As a result, the rate-limiting step is described as the reaction of adsorbed 4NP and hydrogen species on the catalyst surface. Catalyst performance is quantified in terms of the apparent rate constant k_{app} (eq. 1), which is derived from the slope of $ln(C/C_0)$ vs time, where C/C_0 is obtained from the recorded absorbance intensity for **4NP**^{*} at λ_{max} = 400 nm (*A*/*A*₀). The details governing this widely accepted and applied approximation have been discussed in detail in numerous previous publications.^[5]



Scheme 1. Catalytic reduction of 4-nitrophenol (4NP) to 4-aminophenolate (4AP*) by metal nanoparticles under aqueous conditions with excess NaBH₄.

$$-k_{app}t = ln\left(\frac{A}{A_0}\right) = ln\left(\frac{C}{C_0}\right) \tag{1}$$

Here we report a series of materials featuring <10 nm noble metal nanoparticles supported on amorphous carbon black (Au@C, Ag@C, Pt@C and Pd@C). Immobilization of nanoparticles offers several advantages including enhanced stability via inhibition of nanoparticle aggregation, ease of separability and recyclability.^[10] These materials were tested for the reduction of 4NP, and other amino-functionalized nitrophenols (ANPs). The latter are also highly toxic, and used as raw materials or synthetic intermediates in chemical manufacturing.^[11] ANPs can also be viewed as intermediates in the catalytic reduction of dinitrophenols (*high toxicity chemicals*)^[11], thus providing information on functional group (-NH₂) effects that may impact the rate of transformation of multiple $-NO_2$ sites. To both expand the substrate scope of our catalysts, and validate the prognosticating ability of the ubiquitous **4NP** test for selection of the most active species, we explored the

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reduction of common azo dyes methyl red (MR) and methyl orange (MO). Such species can be found in effluent from the industrial manufacture of textiles, paint, plastics, cosmetics, etc. and pose a risk to both human and aquatic health.^[12] Thus, their degradation is also of significant interest. Moreover, they offer the opportunity to compare reactivity of -N=N- moieties, vs. -NO2. While all four materials (Au@C, Ag@C, Pt@C and Pd@C) displayed excellent activity across the entire substrate scope, Pd@C proved to be both remarkably active and highly reusable. Notably, by testing all materials over a broader substrate scope, it becomes evident that the commonly used 4NP reaction does not adequately rank broader catalyst activity. While variance in selectivity across different catalysts is not surprising, it does raise the question of whether performing a single test with 4NP is adequate to select a catalyst to promote to a broader substrate scope

Carbon-supported metal nanoparticles were synthesized by the ascorbic acid-assisted polvol reduction method ^[13]. The metal precursors used for the synthesis of Au, Ag, Pt, and Pd nanoparticles were HAuCl₄, AgNO₃, H₂PtCl₆, and K₂PdCl₄, respectively. Further details are provided in the experimental section. Characterization using transmission electron microscopy (TEM) revealed a relatively uniform dispersion of particles, with a diameter, on average, of < 10 nm; Au@C, 6.79 \pm 1.16 nm; Ag@C, 8.18 ± 2.47 nm; Pt@C, 4.44 ± 0.85 nm; Pd@C, 7.85 ± 1.41 nm (Figures 1, S2). Although the target metal content was 30% w/w, analysis by ICP-MS confirmed values of Pd = 13.5 ± 1.9 %, Pt = 27.8 ± 1.5 %, Au = 6.8 ± 0.9 %, and Ag = 23.5 ± 0.4 %, Analysis by UV-Vis respectively. spectroscopy and thermogravimetric analysis (TGA) is described in the supporting information (Figure S1).



Figure 1. TEM images with particle size distributions in the inset for (A) Au@C, 6.79 ± 1.16 nm; (B) Ag@C, 8.18 ± 2.47 nm; (C) Pt@C, 4.44 ± 0.85 nm; (D) Pd@C, 7.85 ± 1.41 nm.

To investigate the catalytic performance of Au@C, Ag@C, Pt@C and Pd@C, reductions of the ubiquitous 4-nitrophenol (4NP), variably substituted aminonitrophenols 2-amino,5-nitrophenol (2A5NP), 4-amino, 3-nitrophenol (4A3NP), 4-amino, 2-nitrophenol (2A5NP), and common azo dyes methyl orange (MO) and methyl red (MR) were performed (Scheme 2). Reactions were conducted in-situ (1 cm path length quartz UV cell) in deionized water (DIW), with excess NaBH₄ (pH 10.46); see experimental section. In each case (MO excluded), introduction of NaBH₄ to the substrate resulted in brighter colors and red-shifted absorbance due to formation of respective phenolates (4NP*, 2A5NP*, 4A3NP*, and 4A2NP*) or carboxylate (MR*) denoted by "*"(Figure S3). After a to absorbance was recorded, 1 mg of catalyst was added and stirred gently for ~2 s. The reactions were allowed to proceed without further intervention and monitored at fixed intervals by the decreasing absorbance at (4NP*) $\lambda_{max} = 400$ nm, (2A5NP*) $\lambda_{max} =$ 460 nm, (**4A3NP**^{*}) λ_{max} = 510 nm, (**4A2NP**^{*}) λ_{max} = 480 nm, (**MO**) λ_{max} = 466 nm, and (MR*) λ_{max} = 430 nm. All reactions proceeded rapidly with a noted decoloration and appearance of lower intensity absorbances commensurate with the formation of the respective aminophenolates and anilines at $(4AP^*) \lambda_{max} = 310$ nm. (2,5AP*) λ_{max} = 308 nm, (3,4AP*) λ_{max} = 306 nm, (2,4AP*) λ_{max} = 304 nm, (**DMPD**) expected at $\lambda_{max} = -245$ nm and -305 nm^[14] but not observed due to overlap of 4ABS and ABA peaks , (4ABS) λ_{max} = 254 nm^[15], and (ABA) λ_{max} = 310 nm and 240 nm^[16] (Scheme 2, Figures S4-S27). Notably, all catalysts promote hydrolysis of NaBH₄, which leads to a turbid solution, resulting in artificially increased baseline absorbance (up to ~1 a.u.). To extract data under these conditions, the recorded spectra were normalized to either isosbestic points or the baseline. Reactions of Au@C, Ag@C, Pt@C and Pd@C with 4NP, MO, and MR in the absence of NaBH₄ resulted in no shift in absorbance or loss of intensity indicating negligible leaching of metal ions (Figures S30 and S31).



Scheme 2. Substrate scope for catalytic reduction utilizing Au@C, Ag@C, Pt@C and Pd@C.

The obtained kinetic data for the reductions were interpreted according to the Langmuir-Hinshelwood kinetic model, and the data for apparent rate (k_{app}) reported according to eq. 1 (Figure

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2A).^[5a,8] Due to the variance in metal content, and consequent weight % across the four materials, k_{app} is not adequately representative of the activity of the metal nanoparticles, thus hindering a meaningful comparison. Accounting for the metal weight % derived from ICP-MS leads to normalized apparent rate K (min⁻¹g⁻¹; g of metal). The results are graphically interpreted in Figure 2B and detailed in Table 1. While this renders the results self-consistent within the context of this study, direct comparison to previously reported catalysts is complicated by the dependence of k_{app} on a multitude of factors including NaBH₄ concentration, reaction volume, influence of mass transport, temperature and mass of catalyst. Nonetheless, it is accepted that k_{app} as a function of catalyst mass and reaction volume, dubbed "activity parameter" κ (s⁻¹g⁻¹L) can facilitate a useful comparison.^[17]Within that context, focusing on the broadly studied 4NP system, Pd@C, which is unequivocally our most active species (Figure 2, Table 1), exhibits a κ value of 1.67 s⁻¹g⁻¹L. This is comparable to some of the most active Pd-catalysts reported to date, which are consequently among the most active metal species for 4NP conversion. Select examples include but are not limited to: $\kappa = Pd@Fe_3O_4/dextran$ 3.65 s⁻¹g⁻¹L^[17b], Pd@cellulose nanocrystals 1.34 x 10⁻¹ s⁻¹g⁻¹L^[18], Pd@Fe₃O₄/SiO₂ 4.02 x 10⁻¹ s⁻¹g⁻¹L^[19], Pd@C_{amorphous} 3.46 x 10⁻² s⁻¹ ¹g⁻¹L^[20], Pd@organic-frameworks 2.49 s⁻¹g⁻¹L^[21], Pd@TiO₂ 80.6 s⁻¹ ¹g⁻¹L^[22], Pd_{nanowires} 0.19 s⁻¹g⁻¹L (performed at 27 °C)^[23], Pd@RGO 13.04 s⁻¹g⁻¹L^[24].



Figure 2. (A) Observed apparent rate (k_{app}) and (B) apparent rate normalized to weight% of metal (*K*) for the catalytic reduction of substrates presented in Scheme 2 by **Au@C**, **Ag@C**, **Pt@C** and **Pd@C**. (error bars: A = high/low range, B = % error)

Reduction of amino-substituted nitrophenols **2A5NP**, **4A3NP**, and **4A2NP** proceeded in a similar fashion (Figure 2, Table 1). However, *in-situ* data obtained for **Pt@C**, in all instances, was subject to a great deal of noise owing to the high turbidity of the solution as a result of rapid H₂ evolution; measurements were

nonetheless reproducible (Figures S10, S14, and S18). Overall, all catalysts remained effective in the presence of amino functionality, completing the reduction in < 8 min. Switching the reducible functionality from nitro (-NO₂) to azo (-N=N-) with MO and MR as substrates resulted in similarly high activity governed by pseudo-first order kinetics (Figures 3, S20-S27, Table 1). As with the amino-nitrophenol substrates, reactions with Pt@C were more turbid owing to faster H₂ evolution, which ultimately led to greater noise, but nonetheless reproducible data (Figures S22, S26). To rule out possible contribution by carbon black, catalytic degradation of all substrates was conducted under identical conditions (vide supra), with 1 mg carbon black as the active species. Although the reactions progressed under similar pseudofirst order kinetics, the rates obtained, compared to the slowest supported nanoparticle catalyst, were at least 60 x slower (Figures 2B, S28, S29, Table 1).

A common practice with the $4NP \rightarrow 4AP$ reaction is for the selection of top catalyst candidates to be studied with an expanded substrate scope. As can be clearly ascertained from Figure 2B, for **4NP**, the order of performance is Pd@C>>Au@C>>Ag@C≥Pt@C. The simple addition of an amino functionality (2A5NP, 4A3NP, 4A2NP) dramatically alters the ranking established by the model system. While it is not surprising that different catalysts exhibit differing selectivities, it does call into question the prognosticating ability, and suitability of the ubiquitous **4NP** reaction for catalyst selection. By averaging normalized apparent rate K across 4NP and 2A5NP, 4A3NP, 4A2NP we obtain Figure 3 (error bars = std. dev.). Now, the order of performance becomes Pd@C>Au@C≥Pt@C>>Ag@C, and the error bars indicate variance of performance across different functionalities. By expanding the screening to several functionalized substrates, we gain a better understanding of the catalyst performance, with a very minimal penalty in effort. While Pd@C is still the most active species overall, the disparity in performance compared to Au@C and Pt@C is dramatically reduced. Additionally, the large comparative error bars inform us that Pd@C will display significantly different rates in the presence of various amino functionalities, whereas Au@C, Pt@C, and Ag@C will remain largely consistent. Notably, the averaged rates more closely resemble the order of performance for azo dyes MO and MR, with Pd@C displaying the largest variance across the two substrates, as predicted. (Figure 3 inset).





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Table 1. Observed apparent rate (k_{app}) and apparent rate normalized to weight% of metal (*K*) for the catalytic reduction of substrates presented in Scheme 2 by Au@C, Ag@C, Pt@C Pd@C and C.

Substrate	Catalyst	k _{app} (min ⁻¹)	K (min ⁻¹ g ⁻¹)
4NP	с	0.0053	5.3
4NP	Au@C	0.9981 ± 0.0689	14648.86 ± 1011.42
4NP	Ag@C	0.8503 ± 0.0887	3608.06 ± 376.19
4NP	Pt@C	0.8950 ± 0.0651	3219.08 ± 233.99
4NP	Pd@C	4.5394 ± 0.1688	33451.73 ± 1244.75
2A5NP	с	0.0037	3.7
2A5NP	Au@C	0.4037 ± 0.1079	5924.27 ± 1582.91
2A5NP	Ag@C	0.4666 ± 0.0076	1979.82 ± 32.04
2A5NP	Pt@C	2.6586 ± 0.3243	9562.65 ± 1166.32
2A5NP	Pd@C	0.8583 ± 0.0603	6324.61 ± 444.08
4A3NP	С	0.0042	4.2
4A3NP	Au@C	0.2645 ± 0.0024	3881.27 ± 34.88
4A3NP	Ag@C	0.2505 ± 0.0322	1063.00 ± 136.64
4A3NP	Pt@C	1.1412 ± 0.3111	4104.65 ± 1118.83
4A3NP	Pd@C	0.8997 ± 0.0742	6629.70 ± 546.50
4A2NP	С	0.0041	4.1
4A2NP	Au@C	0.4492 ± 0.0745	6592.06 ± 1092.72
4A2NP	Ag@C	0.5179 ± 0.0696	2197.51 ± 295.14
4A2NP	Pt@C	2.7612 ± 0.3688	9931.69 ± 1326.38
4A2NP	Pd@C	0.5389 ± 0.1442	3970.89 ± 1062.28
МО	С	0.0071	7.1
МО	Au@C	0.4962 ± 0.0586	7282.60 ± 860.11
МО	Ag@C	0.5448 ± 0.0534	2311.87 ± 226.60
MO	Pt@C	1.3117 ± 0.0403	4718.11 ± 144.98
МО	Pd@C	3.6840 ± 0.2680	27147.75 ± 1974.92
MR	С	0.0042	4.2
MR	Au@C	0.4517 ± 0.0084	6628.75 ± 122.88
MR	Ag@C	0.5386 ± 0.1176	2285.35 ± 498.83
MR	Pt@C	1.7625 ± 0.1344	6339.61 ± 483.44
MR	Pd@C	1.1350 ± 0.0289	8363.67 ± 212.91

Utilizing identical conditions to the in-situ catalytic trials with 4NP (vide supra), we sought to determine the recyclability and longterm stability of Au@C, Ag@C, Pt@C and Pd@C. After each trial, the turbid solution was allowed to settle overnight, the liquid component carefully decanted, contents washed with DIW, decanted, and the remaining catalyst in the cuvette placed under vacuum overnight. Four subsequent trials were conducted by the addition of 3 mL of DIW containing 4NP and NaBH₄ (Figures S32-S35). By comparing the percent apparent rate (k_{app}) over five trials we can learn more than solely reporting the percent conversion over an ill-defined time frame; further aiding informed catalyst selection (Figure 4). Therein, Au@C experiences the least fluctuation in rate across five trials, signalling that its behaviour is predictable, reproducible, and the catalyst is easily recycled. Pt@C and Ag@C experience a substantial loss in rate after the first trial, which recovers slightly over trials 4 and 5. We attribute this to a combination of mechanical loss, surface restructuring due

to workup and exposure to a reducing environment, adsorption of amine products to surface which may block active sites, and potential leaching. Remarkably, Pd@C, which accounted for the highest rates for 4NP reduction, exhibited a dramatic enhancement in catalytic rate under the recycling protocol (300%+). At the fifth trial, $k_{app} = 21.283 \text{ min}^{-1}$, corresponding to κ = 7.84 s⁻¹g⁻¹L. Repeating a truncated trial with **2A5NP** (3 trials) also revealed modest enhancement of activity for Pd@C, and different levels of decline for the remaining catalysts (Figure S40). We postulate that this results from a combination of factors, including exposure to the reducing environment (NaBH₄) which removes surface bound contaminants (e.g. residual ascorbic acid from synthesis, Figure S1) from Pd@C, thus enhancing catalytic rate.^[25] While the other catalysts are also exposed to a similar protocol, the combination of contaminant removal, and introduction of new species such as aminophenols and boronbased byproducts post reduction has a net deleterious effect.



Figure 4. Percent apparent rate (k_{app}) for the catalytic reduction of **4NP** by **Au@C**, **Ag@C**, **Pt@C** and **Pd@C** over five recycling trials.

In summary, we report a series of noble metal nanoparticles immobilized on amorphous carbon (Au@C, Ag@C, Pt@C and Pd@C). All materials display competitive catalytic activity over paranitrophenol, amino-substituted nitrophenols and azo dyes; Pd@C exhibits especially remarkable activity, which increases further when exposed to recycling protocol. By testing all materials over a broader substrate scope with both added functionalities, and even different reducible moieties, it becomes evident that the commonly used 4NP test reaction does not adequately rank broader catalyst activity. This raises the question, are potentially highly active or selective catalysts being overlooked by an oversimplified screening protocol? Within the narrow scope tested, simply including variably substituted aminonitrophenols more accurately reflects catalyst activity trends when applied to azo functionalities. Our ongoing work focuses on further expanding the scope with the goal of developing a facile screening method that is more broadly predictive.

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Experimental Section

General Methods: All reactions were carried out under air, at ambient temperature (21-23 °C, 45-55% relative humidity). Metal salts HAuCl₄, AgNO₃, H₂PtCl₆, K₂PdCl₄ and Methyl Orange (**MO**) were purchased from Acros Organics. Carbon black (Vulcan XC 72) was purchased from Fuel Cell Store. Ethylene glycol and L-ascorbic acid were purchased from Fisher Scientific. 4-nitrophenol (**4NP**), 4-amino,3-nitrophenol (**4A3NP**), 4-amino,2-nitrophenol (**4A2NP**), 2-amino,5-nitrophenol (**2A5NP**), and NaBH₄ were purchased from TCI America. Methyl Red (**MR**) were purchased from Fisher Scientific. All chemicals were used as received without further purification. UV-Vis Spectra were collected on an Agilent Cary 60 spectrophotometer utilizing 1 cm quartz cuvettes purchased from Spectrocell inc. X-ray photoelectron spectra (XPS) were obtained using a Thermo Scientific ESCALAB Xi+ X-ray Photoelectron Spectrometer with an Al Kα X-ray source (1486.67 eV). pH measurements were conducted with an OHaus 2100 meter with ST210 electrode.

Catalyst Synthesis and Characterization: Carbon-supported metal nanoparticles were synthesized by ascorbic acid-assisted polyol reduction method. The metal precursors used for the synthesis of Au@C, Ag@C, Pt@C, and Pd@C nanoparticles were HAuCl₄, AgNO₃, H₂PtCl₆, and K₂PdCl4 solutions with a metal concentration of 6 mg mL⁻¹, respectively. Typically, 35 mg carbon black was dispersed in 25 mL ethylene glycol by sonicating for 1 h. Then, 2.5 mL of metal precursor solution was added. After stirring for 1 h, the mixture was heated to 120 °C, and 5 ml 0.5 M Lascorbic acid was added dropwise into the solution. The solution was kept at this temperature for 2 h under vigorous stirring. Finally, the catalyst slurry was filtered and washed by copious water and ethanol, and then dried in vacuum at ~21 °C overnight. Actual metal loading was determined by ICP-MS. Dry metal nanoparticles were each digested in 3:1 v/v nitric aid to hydrochloric acid (trace metal grade; Fisher Scientific) overnight at 85 °C. The digests were filtered (0.2 µm pore size) and dissolved Au, Ag, Pt, and Pd quantified using a Thermo Fisher Scientific iCap Qc inductively coupled plasma mass spectrometer with QCell technology and operated in kinetic energy discrimination (KED) mode of analysis with helium as the collision gas. Calibration, internal, and quality control standards (Inorganic Ventures) were prepared in 2% trace metal grade nitric acid (Fisher Scientific). Cysteine (0.5% w/v) was added to the standards and rinse to eliminate adsorption and memory effects. Holmium and bismuth were used as internal references in both standards and samples. TEM images were acquired using a JEOL TEM-1011 operated at 100 kV. TEM samples were prepared by depositing a diluted metal nanoparticle dispersion in ethanol onto copper grids covered with ultrathin carbon films. The size distribution of nanoparticles was obtained by counting over 100 nanoparticles for each sample. TGA of catalysts and support were measured on an ISI TGA-1000 with a 5 cc/min flow of UHP N₂, housed inside a N₂ atmosphere glovebox.

Catalyst testing: Catalytic trials were conducted in a standard 1 cm path length quartz UV cell and monitored in the 225-to-(*up to*)750 nm region, under ambient (-21 °C). In a typical reaction with nitrophenols, 0.39 µmol of reagent was diluted in 1 mL DIW mixed with a 2 mL solution of 0.2 mmol NaBH₄ (pH 10.46); this initial reaction generates the phenolate resulting in a color change from pale to bright yellow, accompanied by a red shift in the UV-Vis (Figure S3). A similar process was utilized for azo dyes (0.34 µmol for **MO** and 0.33 µmol for **MR**); **MO** is not affected by the addition of NaBH₄. After a *t*₀ absorbance was recorded, 1 mg of catalyst was added

and stirred gently for ~2 s. The reaction was allowed to proceed without further intervention and monitored at fixed intervals by the decreasing absorbance at the respective λ_{max} value. Practically, this denotes a color change from bright yellow to colorless. Further details are noted in the Supporting Information.

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Layout 1:

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To pNP or not to pNP? A series of noble metal nanoparticles immobilized on amorphous carbon are reported (Au, Ag, Pt, and Pd). Screening catalytic activity for the reduction of the ubiquitous paranitrophenol, aminonitrophenols, and azo dyes reveals competitive activity across the board, with the Pd species being most active. More importantly, it highlights the limitations of using the benchmark paranitrophenol test as a tool for catalyst selection.

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A broader-scope analysis of the catalytic reduction of nitrophenols and azo dyes with noble-metal nanoparticles

