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Gold Promoted Imine Production
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**Graphic Abstract**

![Chemical reaction diagram](image)

**Highlights**

1. Selective continuous gas phase imine synthesis via reductive coupling.
2. Supported Au exhibits higher selectivity (up to 99%) than benchmark Pd/TiO\textsubscript{2}.
3. \textit{TOF} increased with decreasing Au size (8-3 nm); support oxygen vacancies lower rate.
4. Increased contact time enhanced imine yield.

**Abstract**

The feasibility of gas phase continuous reductive coupling of nitrobenzene and benzaldehyde for imine (\textit{N}-benzylideneaniline) synthesis over oxide (TiO\textsubscript{2}, Fe\textsubscript{2}O\textsubscript{3}, Al\textsubscript{2}O\textsubscript{3}, ZrO\textsubscript{2} and MgO) supported Au and Pd (1.0-3.4\% w/w) has been demonstrated. Reaction over Au/TiO\textsubscript{2} (mean size = 3.2 nm) delivered 99\% selectivity to the target imine. An equivalent level of selectivity was achieved over all the oxide supported Au catalysts with increasing turnover frequency (6 \rightarrow 103 h\textsuperscript{-1}) for smaller Au particles (7.7 \rightarrow 3.2 nm), where nitrobenzene \rightarrow aniline was rate determining. Lower \textit{TOF} over Au/Fe\textsubscript{2}O\textsubscript{3} is linked to the involvement of surface oxygen vacancies that serve to stabilise the nitro-reactant and lower reactivity. Under the same reaction conditions, Pd/TiO\textsubscript{2} exhibited greater H\textsubscript{2} chemisorption capacity and higher
activity but lower imine selectivity ($S = 83\%$) due to toluene formation (via benzaldehyde hydrogenolysis). Reaction at extended contact times ($0.2 \rightarrow 0.5$ s) over Au/TiO$_2$ served to enhance imine yield (to 70\%).

**Keywords:** Gas phase reductive coupling; nitrobenzene; benzaldehyde; imine; supported gold.
1 Introduction

Tandem catalytic coupling processes that combine multiple reactions in one “pot” enhance process efficiency by minimising reaction steps with maximum catalyst utilisation. Tandem coupled systems involving cyclisation [1], cycloaddition [2] and Michael-aldol [3] reactions have drawn on homogeneous catalysis. The requirement for catalyst separation and reuse limits efficiency but this can be circumvented by switching to heterogeneous catalysis. Solid catalysts (β-zeolite [4], NaAlO₂ [5], Rh/Zr-β-zeolite [6] and Pd/MgO [7]) have been used in pressurised (up to 5 bar) batch liquid phase tandem reactions for the synthesis of ethers, glycidol, alkylcyclohexanols and nabumetone. Continuous gas phase operation has clear benefits in terms of reduced downtime and higher throughput but there has been limited work on catalytic tandem reactions [8-10]. We can flag butanol synthesis (13% yield) via a tandem gas phase hydroformylation-hydrogenation of propene and synthesis gas over a SiO₂ supported Ru complex (Shvo catalyst) and supported Rh [8] and ethylene dimerization-isomerization to 2-butene over supported Ni [10].

Imines, widely used as organic intermediates in the manufacture of fine chemicals, pharmaceuticals and agrochemicals [11], are typically prepared in multi-step processes starting with amine synthesis from the corresponding nitro-reactant [12]. Dehydrogenative condensation of alcohols with amines to give imines has been established in liquid phase [13-17] with promising results using supported Au [18,19]. Selectivities up to 99 % have been reported in batch imine synthesis using Au on hydroxyapatite [18] and TiO₂ [19] in coupled reaction of alcohols (benzyl alcohol, cinnamyl alcohol and 1-phenylethanol) with aniline, 1-hexylamine and benzylamine. Oxidative condensation of benzylamines has been studied in liquid phase operation (T = 373 K, P₂O₅ = 5 bar) with exclusivity to imines over (Al₂O₃, TiO₂, carbon and graphite) supported Au [20,21]. The conventional stepwise process (nitro → amine → imine) necessitates multiple reactor operation. Use of nitro-compounds as feedstock
in the coupled system can increase efficiency by incorporating the nitro → amine reduction step (Figure 1, step (I)) within the process. Application of supported Au catalysts in one-pot reductive coupling has not been examined in detail and we could not find any report of nitroarene-aldehyde gas phase conversion. Santos et al. [22] demonstrated one-step synthesis of imine from substituted (vinyl and brominated) nitrobenzene and aromatic aldehydes (benzaldehyde and cinnamaldehyde) over Au/TiO\textsubscript{2} in batch liquid phase (\( T = 393 \) K, \( P_{H_2} = 4\text{-}12 \) bar). Here we evaluate the viability of imine production by gas phase continuous reductive coupling of nitrobenzene and benzaldehyde (as model reactants) over Au. As illustrated in Figure 1, nitrobenzene reduction determines imine production by supplying aniline for condensation. In prior work, we have shown that Au particle size and support redox character play crucial roles in determining catalytic activity in –NO\textsubscript{2} reduction [23]. Moreover, control over contact time in continuous operation can govern conversion and reaction rate in selective hydrogenation [24] where increased residence time resulted in elevated conversion in benzonitrile → benzylamine [25] and furfural → 2-methylfuran [26]. In this study, we consider these factors and examine the performance of Au on a series of oxides (TiO\textsubscript{2}, Fe\textsubscript{2}O\textsubscript{3}, Al\textsubscript{2}O\textsubscript{3}, ZrO\textsubscript{2} and MgO). Supported Pd is used commercially in nitrobenzene hydrogenation [27]. As selective nitroarene adsorption via the –NO\textsubscript{2} function on TiO\textsubscript{2} and at the metal-TiO\textsubscript{2} interface serves to enhance amine production rate [28], we have adopted Pd/TiO\textsubscript{2} as a benchmark.

2 Experimental

2.1 Catalyst Preparation and Activation

The supports used were commercial (TiO\textsubscript{2} (P25, Degussa), Al\textsubscript{2}O\textsubscript{3} (Puralox, Condea Vista) and MgO (Sigma-Aldrich)) or synthesised (Fe\textsubscript{2}O\textsubscript{3} and ZrO\textsubscript{2}) following procedures described elsewhere [29,30]. Gold on MgO was prepared by impregnation of MgO (10 g, Sigma Aldrich, >99%) with aqueous H\textsubscript{Au}Cl\textsubscript{4} (5 × 10\textsuperscript{-2} M, 50 cm\textsuperscript{3}, Sigma-Aldrich, 99%). The
slurry was heated (at 2 K min\(^{-1}\)) to 353 K under vigorous stirring (600 rpm) and maintained in a He purge for 5 h. Gold on TiO\(_2\), Fe\(_2\)O\(_3\), Al\(_2\)O\(_3\) and ZrO\(_2\) was synthesised by deposition-precipitation with urea (Riedel-de Haën, 99%) as basification agent. An aqueous solution of urea (100-fold excess) and HAuCl\(_4\) (3-7 \(\times\) 10\(^{-3}\) M, 400 cm\(^3\)) was added to the support (10-30 g). The suspension was stirred (600 rpm) and heated (at 2 K min\(^{-1}\)) to 353 K, where the pH progressively increased to 6-8 after 3-4 h as a result of urea decomposition [31]. The solid obtained was separated by filtration, washed with distilled water and dried in 45 cm\(^3\) min\(^{-1}\) He at 373 K for 5 h. A supported Pd benchmark was prepared by precipitation of Pd(NO\(_3\))\(_2\) (4 \(\times\) 10\(^{-3}\) M, 300 cm\(^3\), Sigma-Aldrich, 99%) on TiO\(_2\) (10 g), adding aqueous Na\(_2\)CO\(_3\) (2 M, Riedel-de Haën, 99%) dropwise until pH >10 [32]. The slurry was heated (at 2 K min\(^{-1}\)) to 353 K and maintained for 4 h. The solid was separated by filtration, washed with distilled water and dried under vacuum at 333 K for 12 h. The catalyst precursors were sieved (ATM fine test sieves) to mean particle diameter = 75 \(\mu\)m. Samples were activated in 60 cm\(^3\) min\(^{-1}\) H\(_2\) at 2-5 K min\(^{-1}\) to 423-603 K and passivated at ambient temperature in 1% v/v O\(_2\)/He for ex situ characterisation.

### 2.2 Catalyst Characterisation

Metal content was measured by atomic absorption spectroscopy using a Shimadzu AA-6650 spectrometer with an air-acetylene flame from the diluted extract in aqua regia (25% v/v HNO\(_3\)/HCl). Temperature programmed reduction (TPR) and H\(_2\) chemisorption were conducted on the commercial CHEM-BET 3000 (Quantachrome Instrument) unit equipped with a thermal conductivity detector (TCD) for continuous monitoring of gas composition and the TPR Win\(^{\text{TM}}\) software for data acquisition/manipulation. Samples were loaded into a U-shaped Pyrex glass cell (3.76 mm i.d.) and heated in 17 cm\(^3\) min\(^{-1}\) (Brooks mass flow controlled) 5% v/v H\(_2\)/N\(_2\) at 2-5 K min\(^{-1}\) to 423-603 K, which was maintained until the signal returned to baseline. The activated sample was swept with 65 cm\(^3\) min\(^{-1}\) N\(_2\) for 1.5 h, cooled
to reaction temperature (413 K) and subjected to H\textsubscript{2} pulse (10 µl) titration. In blank tests, there was no measurable H\textsubscript{2} uptake on the support alone. Oxygen chemisorption post-TPR was employed to determine the extent of support reduction, where samples were reduced as described above, swept with 65 cm\textsuperscript{3} min\textsuperscript{-1} He for 1.5 h, cooled to 413 K with pulse (50 µl) O\textsubscript{2} titration. It has been demonstrated that Au contribution to total O\textsubscript{2} adsorbed is negligible [33].

Nitrogen adsorption-desorption isotherms were obtained using the commercial Micromeritics Gemini 2390p system. Prior to analysis, the samples were outgassed at 423 K for 1 h in N\textsubscript{2}. Total specific surface area (SSA) was obtained using the standard BET method. Metal particle morphology (size and shape) was examined by scanning transmission electron microscopy (STEM, JEOL 2200FS), employing Gatan Digital Micrograph 1.82 for data acquisition/manipulation. Samples for analysis were prepared by dispersion in acetone and deposited on a holey carbon/Cu grid (300 Mesh). The surface area weighted mean metal size \(d_{STEM}\) was based on a count of at least 300 particles according to

\[
d_{STEM} = \frac{\sum i n_i d_i^3}{\sum i n_i d_i^2}
\]

where \(n_i\) is the number of particles of diameter \(d_i\).

2.3 Catalytic Procedure

Catalyst testing was carried out at atmospheric pressure and 413 K \textit{in situ} after activation in a continuous flow fixed bed tubular reactor (i.d. = 15 mm). The catalytic reactor has been described elsewhere [29,30,34] but features pertinent to this study are given below. A layer of borosilicate glass beads served as preheating zone where the reactant was vaporised and reached reaction temperature before contacting the catalyst bed. Isothermal conditions (±1 K) were maintained by diluting the catalyst bed with ground glass (75 µm), which was mixed thoroughly with the catalyst before loading into the reactor. Reaction temperature was
continuously monitored by a thermocouple inserted in a thermowell within the catalyst bed. The reactant(s) (benzaldehyde and/or nitrobenzene) was(were) delivered as an ethanolic solution to the reactor via a glass/teflon air-tight syringe and teflon line using a microprocessor controlled infusion pump (Model 100 kd Scientific) at a fixed calibrated flow rate. A co-current flow of organic reactant(s) and H$_2$ was maintained at a reactor contact time ($\tau = 1/$GHSV) in the range 0.2 - 0.5 s. The molar metal to inlet organic molar feed rate ($n/F$) spanned the range $1.3 \times 10^{-3} - 5.8 \times 10^{-2}$ h. In blank tests, passage of each reactant (and mixture) in a stream of H$_2$ through the empty reactor or over each support did not result in any detectable conversion. The reactor effluent was condensed in a liquid N$_2$ trap for subsequent analysis using a Perkin-Elmer Auto System XL gas chromatograph equipped with a programmed split/splitless injector and a flame ionisation detector, employing a DB-1 (50 m × 0.33 mm i.d., 0.20 μm film thickness) capillary column (J&W Scientific). Data acquisition and manipulation were performed using the Turbochrom Workstation (Version 6.3.2) chromatography data system. Nitrobenzene (Riedel-de Haën, ≥99%), aniline (Riedel-de Haën, ≥99%), benzaldehyde (Fluka, ≥98%), benzyl alcohol (Riedel-de Haën, ≥99%), toluene (Fisher Chemicals, >99%), N-benzylideneaniline (Sigma Aldrich, 99%), N-benzylaniline (Sigma Aldrich, 99%) and ethanol (Sigma Aldrich, ≥99%) were used without further purification. All the gases (H$_2$, O$_2$, N$_2$ and He) were of high purity (>99.98%, BOC). Reactant (i) fractional conversion ($X$) is defined by

$$X_i = \frac{[reactant]_{i,\text{in}} - [reactant]_{i,\text{out}}}{[reactant]_{i,\text{in}}}$$  \hspace{1cm} (2)

and selectivity ($S$) to product “$j$” is given by

$$S_j(\%) = \frac{[product]_{j,\text{out}}}{[reactant]_{i,\text{in}} - [reactant]_{i,\text{out}}} \times 100$$  \hspace{1cm} (3)

Yield ($Y$) to product “$j$” was obtained from

$$Y_j(\%) = \frac{[product]_{j,\text{out}}}{[reactant]_{i,\text{in}}} \times 100$$  \hspace{1cm} (4)
where subscripts “in” and “out” refer to the inlet and outlet gas streams, respectively. Catalytic activity is also quantified in terms of reactant consumption rate \( R, \text{ mol}_{\text{reactant}} \text{ mol}_{\text{metal}}^{-1} \text{ h}^{-1} \) [35] and turnover frequency \( \text{TOF}, \text{ rate per metal site} \) calculated using

\[
\text{TOF} \ (\text{h}^{-1}) = \frac{R}{D}
\]

where \( D \) represents the metal dispersion (surface to total metal atoms) obtained from STEM measurements, considering metal nanoparticles with spherical morphology [30]. Repeated reactions with different samples from the same batch of catalyst delivered raw data reproducibility better than \( \pm 6\% \) with a carbon mass balance \( \geq 95\% \).

3 Results and Discussion

3.1 Au/TiO2 vs. Pd/TiO2

3.1.1 Catalyst Characterisation

The physicochemical properties of TiO2 supported Au and Pd are given in Table 1. Both catalysts had the same SSA (52-53 m² g⁻¹). The TPR profile for Au/TiO2 (Figure 2(A)) displayed a positive peak at 373 K where H₂ consumption exceeded that required for the Au³⁺ → Au⁰ step (see Table 1), suggesting partial support reduction [36]. A single TPR peak \( T_{\text{max}} = 350-408 \) K has been recorded elsewhere during activation of Au/TiO₂ and attributed to combined Au precursor reduction and Ti⁴⁺ → Ti³⁺ conversion at the metal/support interface [37]. The TPR profile of Pd/TiO₂ (Figure 2(B)) is characterised by a negative (H₂ release) signal at \( T_{\text{max}} = 350 \) K and a positive (H₂ consumption) peak at \( T_{\text{max}} = 566 \) K, consistent with results reported by Babu et al. [32]. The lower temperature peak can be attributed to Pd hydride decomposition. Palladium absorbs H₂ at ambient temperature and pressures >0.02 atm (0.05 atm in this study) to form a hydride [38], which is thermally unstable and decomposes during TPR at 331-353 K [32,39]. Hydride composition (H/Pd) shows a dependence on Pd size where the value obtained in this work (=0.28 mol mol⁻¹) falls within
the range (0.10-0.52) characteristic of a 2-10 nm Pd particle size [40]. The positive signal at higher temperature can be attributed to reduction of oxidised Pd and/or partial support reduction [32]. Metal particle morphology (size and shape) was evaluated by STEM; representative images and associated particle size histograms are provided in Figure 3. Both catalysts displayed quasi-spherical particles with similar size distributions and surface area weighted mean (3.2-3.4 nm). Metal particle size can impact on catalytic hydrogenation, particularly in the case of Au catalysts where particles <10 nm have been identified as critical for hydrogen activation [41] and hydrogenation activity [33]. Hydrogen chemisorption under reaction conditions (413 K) is given in Table 1 where uptake on Au/TiO₂ was appreciably lower than Pd/TiO₂, in line with relevant literature [42] and resulting from the lower H₂ dissociation energy barrier on Pd due to the unfilled d band [33,42].

3.1.2 Catalysis Results

The tandem coupling process requires a catalyst that promotes the reduction of nitrobenzene to aniline (Figure 1, step (I)) and circumvents benzaldehyde hydrogenation (step (IV)) and/or hydrogenolysis (steps (V) and (VI)) to ensure aniline + benzaldehyde supply for subsequent condensation (step (II)). We first investigated stand-alone hydrogenation of nitrobenzene and benzaldehyde over Au/TiO₂ and Pd/TiO₂; the results are presented in Table 2. Nitrobenzene conversion over both catalysts generated aniline as sole product. Benzaldehyde hydrogenation over Au/TiO₂ was fully selective to benzyl alcohol whereas Pd/TiO₂ favoured hydrogenolysis to toluene (selectivity = 95%). Supported Pd was appreciably more active than Au/TiO₂ in both reactions and this can be linked to the greater H₂ chemisorption capacity (Table 1). Higher nitro-group conversion is consistent with reaction thermodynamics where nitrobenzene → aniline (ΔG₄₁₃ K = -436 ± 1 kJ mol⁻¹) is more favourable than benzaldehyde hydrogenation (to benzyl alcohol, ΔG₄₁₃ K = -24 ± 2 kJ mol⁻¹) or hydrogenolysis (to toluene, ΔG₄₁₃ K = -108 ± 3 kJ mol⁻¹). The prerequisite for aniline
formation was met by both catalysts but undesired benzaldehyde hydrogenolysis was promoted over Pd/TiO$_2$.

Temporal variation of conversion and product selectivity in nitrobenzene + benzaldehyde reductive coupling over Au/TiO$_2$ (A) and Pd/TiO$_2$ (B) is presented in Figure 4. In both cases, we detected an increase in activity and formation of target imine as principal product to attain steady state after 1 h on-stream. This result demonstrates a successful continuous tandem reaction. We could not find any directly comparable work but it should be noted that the highest imine selectivity (93%) reported in liquid phase reductive coupling of nitrobenzene + benzaldehyde over Au/TiO$_2$ [22] is lower than that achieved in this study (99%). Arai et al. [43] reported formation of amine and benzyl alcohol as significant by-products (imine selectivity ≤80%) for reaction over Pt/Al$_2$O$_3$. Kyriakou et al. [44] recorded Au leaching during the liquid phase coupling of iodobenzene and phenylacetylene over Au/TiO$_2$ and Au/SiO$_2$. Our results in continuous gas operation represent an advancement over batch liquid systems. Activity in the tandem reaction over Au/TiO$_2$ coincided with stand-alone nitrobenzene reduction ($R = 32$ h$^{-1}$ vs. 30 h$^{-1}$), suggesting that imine formation in the coupled system was controlled by the nitrobenzene $\rightarrow$ aniline step. Liu et al. [17] noted that the hydrogenation of nitrobenzene to aniline was much slower than aniline condensation with benzaldehyde. Lower activity in the tandem reaction over Pd/TiO$_2$ relative to stand-alone nitrobenzene conversion ($R = 93$ h$^{-1}$ vs. 1136 h$^{-1}$) must result from competition between benzaldehyde and nitrobenzene reactants where hydrogenolysis to form toluene limits imine production ($S_{\text{imine}} = 83\%$). Au/TiO$_2$ exhibits low activity for (undesired) benzaldehyde hydrogenation and selective imine production was governed by the nitrobenzene hydrogenation rate. Nitro-group reduction over supported Au is influenced by support redox properties [45] and Au particle size [46]. We probed these effects by examining the catalytic action of Au (of varying size) on reducible and non-reducible carriers.
3.2 Oxide Supported Au

3.2.1 Catalyst Characterisation

The SSA recorded (in Table 1) for the supported Au catalysts range from 24 m² g⁻¹ (Au/MgO) to 166 m² g⁻¹ (Au/Al₂O₃) and fall within values reported in the literature [47-50]. The TPR profiles (Figure 5) exhibit a single H₂ consumption peak and $T_{max}$ in the range 363-512 K (Table 1), as reported elsewhere [47,51,52]. Hydrogen consumption during TPR showed a dependency on support redox character where values recorded for Au on non-reducible oxides (Au/Al₂O₃ and Au/ZrO₂) matched the amount required for metal precursor reduction (Table 1). The appreciably lower consumption during TPR of Au/MgO can be attributed to metal reduction (pre-TPR) during catalyst preparation and drying [53]. Excess H₂ consumption for Au/Fe₂O₃ can be ascribed to partial reduction of the support, which was further confirmed by O₂ chemisorption post-TPR where uptake on Au/Fe₂O₃ (and Au/TiO₂ to a lesser extent) indicates formation of oxygen vacancies during TPR [54,55]. Gold particle size histograms are provided in Figure 6. The mean Au sizes (Table 1) reveal a dependence of metal dispersion on oxide reducibility. Smaller Au particles were formed on reducible Fe₂O₃ and TiO₂ where oxygen vacancies have a stabilising effect and inhibit sintering [56]. The largest mean size (7.7 nm) associated with Au/MgO (1-15 nm) is the result of synthesis by less controlled impregnation that is known to result in weaker precursor/support interactions leading to particle agglomeration during activation [57]. Okumura et al. [58] reported that Au/Al₂O₃ (1% wt.) prepared by deposition-precipitation and impregnation exhibited mean Au particle sizes of 2.5 nm and 37 nm, respectively. Hydrogen adsorption (Table 1) under reaction conditions (413 K) was highest on Au/Al₂O₃ (318 µmol g⁻¹) and lowest for Au/MgO (26 µmol g⁻¹). There is a consensus that H₂ chemisorption is favoured on smaller (2-10 nm) Au particles that possess a higher fraction of low coordinated Au atoms at corner and edge sites [59]. Hydrogen dissociated on Au can spill over onto the support [60-
where a larger surface area accommodates greater quantities of surface hydrogen [63]. Hydrogen uptake can be linked to SSA (Au/Al_2O_3 > Au/TiO_2 ≈ Au/ZrO_2 > Au/Fe_2O_3 > Au/MgO). Any effect due to the greater SSA of Au/ZrO_2 relative to Au/TiO_2 must be offset by the larger Au particles on ZrO_2.

### 3.2.2 Catalysis Results

Turnover frequencies (TOF) and imine selectivity in the reductive coupling of nitrobenzene with benzaldehyde are presented in Figure 7. High (97-99%) selectivity to imine with trace amine formation was common to all the Au catalysts with no evidence of benzyl alcohol and/or toluene formation. As a general observation, TOF increased (6 → 103 h^{-1}) with decreasing (7.7 → 3.2 nm, Au/MgO < Au/ZrO_2 < Au/Al_2O_3 < Au/TiO_2) mean Au size. This response finds agreement with prior work showing sympathetic structure sensitivity for the hydrogenation of nitroarenes over supported Au [23] but we provide here the first evidence that this effect extends to tandem reactions. It should be noted that Au/Fe_2O_3 with the smallest mean Au size (2.9 nm) and greatest oxygen vacancy density (*i.e.* highest O_2 chemisorption, Table 1) deviates from this trend. This can be tentatively attributed to stronger binding of the nitro-group at vacancy sites that inhibits –NO_2 reactivity [64]. Moreover, loss of metal character for smaller Au nano-particles, which applies in particular to Au/Fe_2O_3 (40% particles <2 nm) has been shown to result in lower intrinsic hydrogenation activity [65]. Higher TOF can be linked to greater H_2 chemisorption capacity (26 → 146 µmol g_{Au}^{-1}, Au/MgO < Au/Fe_2O_3 < Au/ZrO_2 < Au/TiO_2). However, reaction over Au/Al_2O_3 with the highest H_2 uptake (318 µmol g_{Au}^{-1}) delivered a lower TOF than Au/TiO_2. Nitro-group polarisation plays a critical role in determining reaction rate and application of the selective energy transfer (SET) has established enhanced –NO_2 activation at TiO_2 and/or Au-TiO_2 interfacial sites [66]. Boronat *et al.* [28], studying the hydrogenation of nitrostyrene by *in situ* IR analysis and quantum chemical calculations, attributed higher TOF (to aminostyrene) over
Au/TiO\textsubscript{2} compared with Au/SiO\textsubscript{2} to –NO\textsubscript{2} activation at the Au-TiO\textsubscript{2} interface. A high Au dispersion on TiO\textsubscript{2} serves to extend the Au-TiO\textsubscript{2} interface and can contribute to increased TOF. The specific rate of the tandem reactions converged with that recorded for nitrobenzene hydrogenation for all the catalysts (Figure 7), further demonstrating nitrobenzene → aniline as rate determining.

The tests to this point have established structure sensitivity in imine production over Au with the highest specific activity for Au/TiO\textsubscript{2} (Figure 7). However, productivity in terms of yield ($Y_{\text{imine}} = 30\%$) was still low. We considered the possibility of increasing contact time ($\tau$) as a means of enhancing imine yield in sequential hydrogenation-condensation over Au/TiO\textsubscript{2}. Higher $\tau$ (0.2 → 0.5 s) resulted in a three-fold increase in activity with an imine selectivity and yield of 93\% and 70\%, respectively. The marginal drop in selectivity ($S_{\text{imine}} = 99\% \rightarrow 93\%$) was due to amine formation ($S_{\text{amine}} = 0\% \rightarrow 7\%$) via consecutive hydrogenation of the imine. There is the possibility that competition for the same sites in the hydrogenation of imine (Figure 1, step (III)) and nitrobenzene → aniline (step (I)) impacts on product distribution. A mixed feedstock of nitrobenzene/$N$-benzylideneaniline was used to probe this effect and the consumption rates for each reactant over Au/TiO\textsubscript{2} as a function of inlet reactant ratio can be compared in Figure 8. Nitrobenzene hydrogenation rates (26-45 mol–NO\textsubscript{2} molAu\textsuperscript{-1} h\textsuperscript{-1}) were appreciably greater than imine hydrogenation (2-14 mol–C=\textsuperscript{N} molAu\textsuperscript{-1} h\textsuperscript{-1}) at each nitrobenzene/imine ratio. This suggests preferential –NO\textsubscript{2} group (relative to –C=\textsuperscript{N}) activation/reduction. As imine content in the feed was increased, nitrobenzene hydrogenation rate was lowered with a concomitant increase in imine consumption. This can account for amine production at higher conversions in the coupled reaction.

4 Conclusions

Nano-scale Au (mean = 2.9-7.7 nm) on a series of oxide (TiO\textsubscript{2}, Fe\textsubscript{2}O\textsubscript{3}, Al\textsubscript{2}O\textsubscript{3}, ZrO\textsubscript{2} and MgO) supports generated high selectivity (97-99\%) to the target imine ($N$-
benzylideneaniline) in the continuous gas phase reductive coupling of nitrobenzene and benzaldehyde. Under the same reaction conditions, Pd/TiO₂ (mean Pd size = 3.4 nm) delivered higher activity but generated toluene (from benzaldehyde hydrogenolysis) as significant by-product, resulting in lower imine selectivity (83%). Turnover frequencies (6 → 103 h⁻¹) were dependent on Au size where a rate increase with decreasing Au size (7.7 → 3.2 nm) can be linked to greater H₂ chemisorption capacity under reaction conditions (413 K) for smaller Au particles. Lower TOF over Au (mean = 2.9 nm) on reducible Fe₂O₃ is attributed to a binding of the nitro group to surface oxygen vacancies that suppresses reactivity. Activity in the coupled reaction coincided with stand-alone nitrobenzene hydrogenation, suggesting that the latter is rate-determining. Increasing contact time (0.2 → 0.5 s) over Au/TiO₂ served to further enhance imine yield (30% → 70%). High imine selectivity in continuous operation at ambient pressure represents a significant advancement over current pressurised batch liquid operations.

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**References**

87-97.


**Figure captions**

**Figure 1**: Reaction scheme for the reductive coupling of nitrobenzene with benzaldehyde.

**Figure 2**: Temperature programmed reduction (TPR) profiles for (A) Au/TiO₂ and (B) Pd/TiO₂.

**Figure 3**: (I) Representative STEM images with (II) associated metal particle size distribution histograms for (A) Au/TiO₂ and (B) Pd/TiO₂.

**Figure 4**: Variation of nitrobenzene fractional conversion (X, ■) and product selectivity (S, □: imine, ○: toluene and △: aniline) with time on-stream in the reductive coupling of nitrobenzene + benzaldehyde over (A) Au/TiO₂ and (B) Pd/TiO₂. *Reaction conditions*: \( T = 413 \, \text{K}; \, n/F = 3.3 \times 10^{-3} - 8.5 \times 10^{-3} \, \text{h}. \)

**Figure 5**: Temperature programmed reduction (TPR) profiles for (A) Au/Fe₂O₃, (B) Au/Al₂O₃, (C) Au/ZrO₂ and (D) Au/MgO.

**Figure 6**: Metal particle size distribution histograms for (A) Au/Fe₂O₃, (B) Au/Al₂O₃, (C) Au/ZrO₂ and (D) Au/MgO.

**Figure 7**: Turnover frequency (TOF) in terms of aniline (in stand-alone hydrogenation of nitrobenzene, hatched bar) and imine (in the coupled reaction, solid bar) formation and selectivity to imine in the coupled system (■) over oxide supported Au catalysts. *Reaction conditions*: \( T = 413 \, \text{K}; \, P = 1 \, \text{atm}. \)

**Figure 8**: Nitrobenzene (solid bar) and imine (open bar) consumption rate as a function of inlet nitrobenzene/imine molar ratio for the hydrogenation of nitrobenzene + imine mixtures over Au/TiO₂. *Reaction conditions*: \( T = 413 \, \text{K}; \, P = 1 \, \text{atm}. \)
Figure 1
Figure 2

(A) TCD signal (a.u.)

(B) TCD signal (a.u.)

$T$ (K)

$t$ (h)

× 2
Figure 3

(AI) 10 nm

(AII) Particle Size Range (nm)

(BI) 10 nm

(BII) Particle Size Range (nm)
Figure 4

(A) $X_{\text{nitrobenzene}}$ vs. $t$ (h)

(B) $X_{\text{nitrobenzene}}$ vs. $t$ (h)
Figure 5

(A) 

(B) 

(C) 

(D)
Figure 6

(A) 

(B) 

(C) 

(D)
Figure 7
Figure 8
Table 1: Physicochemical characteristics of oxide supported Au and Pd catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Au/TiO₂</th>
<th>Pd/TiO₂</th>
<th>Au/Fe₂O₃</th>
<th>Au/Al₂O₃</th>
<th>Au/ZrO₂</th>
<th>Au/MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal loading (% w/w)</td>
<td>1.9</td>
<td>1.1</td>
<td>1.0</td>
<td>1.1</td>
<td>1.0</td>
<td>3.4</td>
</tr>
<tr>
<td>SSA (m² g⁻¹)</td>
<td>52</td>
<td>53</td>
<td>38</td>
<td>166</td>
<td>93</td>
<td>24</td>
</tr>
<tr>
<td>TPR T_max (K)</td>
<td>373</td>
<td>350, 566</td>
<td>363</td>
<td>451</td>
<td>476</td>
<td>512</td>
</tr>
<tr>
<td>H₂ TPR (µmol g⁻¹)</td>
<td>170⁹/147⁸b</td>
<td>34⁹/99⁹b</td>
<td>593⁹/74⁹b</td>
<td>87⁹/84⁹b</td>
<td>56⁹/61⁹b</td>
<td>5⁹/256⁹b</td>
</tr>
<tr>
<td>H₂ uptake (µmol g⁻¹)</td>
<td>146</td>
<td>5015</td>
<td>76</td>
<td>318</td>
<td>137</td>
<td>26</td>
</tr>
<tr>
<td>Mean size (dSTEM) ± σ² (nm)</td>
<td>3.2 ± 1.0</td>
<td>3.4 ± 1.1</td>
<td>2.9 ± 0.9</td>
<td>4.3 ± 1.6</td>
<td>7.0 ± 1.8</td>
<td>7.7 ± 3.5</td>
</tr>
<tr>
<td>O₂ uptake (µmol g⁻¹)</td>
<td>8</td>
<td>-</td>
<td>168</td>
<td>1</td>
<td>3</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

* consumption during TPR; btheoretical for Au³⁺ → Au⁰ (or Pd²⁺ → Pd⁰); cchemisorption at 413 K.

Table 2: Reaction rate (R, h⁻¹), fractional conversion (X) and product selectivity (S_product, %) in stand-alone hydrogenation of nitrobenzene and benzaldehyde over Au/TiO₂ and Pd/TiO₂; Reaction conditions: T = 413 K; P = 1 atm; τ = 0.2 s.

<table>
<thead>
<tr>
<th>Reactant(s)</th>
<th>Catalyst</th>
<th>R (h⁻¹)</th>
<th>X (-)</th>
<th>S_aniline (%)</th>
<th>S_benzyl alcohol (%)</th>
<th>S_toluene (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrobenzene</td>
<td>Au/TiO₂</td>
<td>30</td>
<td>0.1</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Pd/TiO₂</td>
<td>1136</td>
<td>0.1</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>Au/TiO₂</td>
<td>6</td>
<td>0.5</td>
<td>-</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Pd/TiO₂</td>
<td>68</td>
<td>0.5</td>
<td>-</td>
<td>5</td>
<td>95</td>
</tr>
</tbody>
</table>